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peri INTERACTION IN NAPHTHALENE DERIVATIVES

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I. INTRODUCTION

In the naphthalene molecule, the 1- and 8-positions are said to be *peri* to each other (I). In view of the geometry of naphthalene, substituents located at these positions are in much closer proximity than similar substituents located *ortho* to each other. This closer proximity has been responsible for the appearance of several unique properties of *peri*-substituted naphthalenes. Such "proximity effects" have been reported by several workers over many years, and this aspect of naphthalene chemistry has attracted increasing attention in recent years. The present review is an attempt to collect the available data on *peri* interactions in naphthalene derivatives as revealed by physical and chemical methods.

Though several polynuclear systems, such as 4,5-dimethylphenanthrene and benzo[*c*]phenanthrene, can

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be formally considered as *peri*-substituted naphthalenes, this review is restricted mainly to *peri* interactions in naphthalene derivatives alone because of the vast amount of data available on this single group of compounds. However, an occasional excursion into other systems is made where this appeared to be profitable for the discussion at hand. Though a number of references to studies on other systems are included, a complete account of them is deliberately avoided. The preparation of *peri*-substituted naphthalenes is not discussed except to illustrate some steric or electronic effect. The terms C_8-hydrogen, *peri*-methine, and *peri*-hydrogen are used synonymously in this paper.

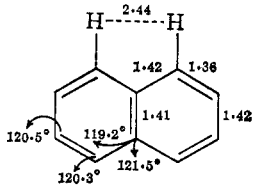
The literature survey is complete up to date as of June 1965, and, wherever possible, later references are also included. Every effort has been made to bring together most of the related work in this field. However, no pretense to completeness is possible because of the widely scattered literature.

II. Physical Evidence for *peri* Interaction

A. Crystal Structure

Steric strain due to bulky substitution at interfering positions can be relieved by (a) stretching of bonds, (b) in-plane deflection of the substituent, (c) out-of-plane deflection of the substituent, and (d) a distortion or buckling of the nucleus itself. Of these possibilities, (a) is practically excluded because of the large amounts of energy associated with even a small change in bond length. All of the other modes for relief of steric compression may come into play in overcrowded organic molecules. Whether one or more of these operate in any given molecule depends on the extent of steric compression in that molecule. The relief of strain by a multiplicity of these atomic motions is referred to as "decentralization of steric strain" (30) or "distribution of deformation over many coordinates" (145). While in many cases considerable in-plane and out-of-plane deviations of the exocyclic bonds occur, reported cases of nuclear distortions are relatively limited. It is, however, noteworthy that a relatively large relief of steric interaction is achieved even by slight molecular distortions. In such molecules two competing influences are in operation, namely, the loss in resonance energy due to nuclear distortions and deviations of substituents from the mean molecular plane on the one hand, and the decrease in steric strain energy on the other. Resonance of the substituent with the aromatic skeleton strives to keep the molecule planar, and steric repulsion due to nonbonded atoms tends to cause deviation from planarity.

The unsubstituted naphthalene molecule is known to have a rigidly planar structure (146). The bond lengths and bond angles in naphthalene have been accurately determined (151) and the distance between



I

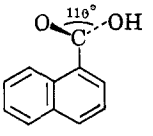
the *peri*-carbon atoms is only about 2.4–2.5 A. In aromatic molecules, the normal nonbonded H···H distance is 2.4–2.5 A, and the nonbonded C···C distance is ~3.0 A. It is therefore logical to expect that with substituents other than hydrogen[2] at the *peri* positions in naphthalene there will be considerable steric interaction. A number of crystallographic studies have been made on 1-monosubstituted and 1,8-disubstituted naphthalene derivatives which throw considerable light on the nature of *peri* interaction in these molecules and the mechanism by which the steric strain is overcome. Such studies also help to arrive at a quantitative picture of nonbonded repulsion energies in organic molecules (28, 153, 274). This section of the review concerns itself with the results obtained from crystal-structure studies of naphthalene derivatives containing possible *peri* interactions. Newman and Wise (447) and more recently Ferguson and Robertson (196) have summarized some of these results.

Even though the situation with respect to crystal structure of heavily substituted benzene derivatives is not clear (196, 226, 230, 256), the case of naphthalene derivatives seems to be fairly well understood. In 1-substituted naphthalenes, the substituent undergoes in-plane and/or out-of-plane deformations because of *peri*-hydrogen interaction. The 2-substituted isomers would be expected to be planar. 2-Naphthoic acid (545) and 2,6-dichloronaphthalene (322) are in fact found to be planar. Surprisingly, however, in 2,6-diphenylnaphthalene the phenyl substituents are twisted by 25° from the naphthalene plane in contrast to biphenyl which is believed to be planar in the solid state (323). In 1,3-dichloro- (547) and 1,4-dibromonaphthalene (546), the α-halo substituents undergo significant deviations (~0.3–0.4 A) from the mean naphthalene plane.

When the 1-substituent is bulkier, there are more significant changes. For example, Trotter (544) has found that in 1-naphthoic acid (II) the carboxyl group is twisted out of plane, with the oxygen atoms lying at mean distances of 0.2 A, one above and the other below the mean plane. The interplanar angle is 12°. This relieves the strain only partly. There occurs in addition a slight in-plane displacement of the C_{Ar}–CO_2H bond away from the *peri* position and a reduction of the OCO angle to 110° from the normal

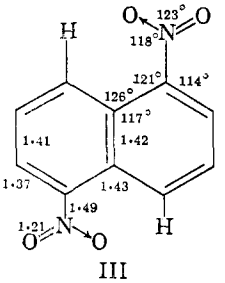
(2) For a suggestion that even with hydrogen at both *peri* positions there is a positive interference with the normal molecular conformation, see ref 151, 153, 494.

value of ~120°. When the 1-substituent is even more bulky as in 1,1′-binaphthyl, the interplanar angle is 73° (106).

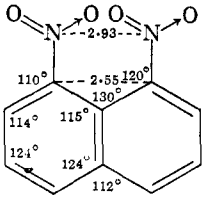


II

In an earlier X-ray investigation (514) of 1,5-dinitronaphthalene (III), only a single projection analysis was made. It was believed to indicate the rather improbable planar structure for this molecule. In a more thorough investigation, Trotter (543) has shown that the molecule as a whole deviates considerably from planarity even though the naphthalene ring itself remains planar. The nitro groups are twisted by 49° from the plane of the nucleus by rotation about the C–N bond. There is also a considerable displacement of the C–N bonds within the molecular plane, leading to a reduction of the exocyclic valency angles to 114°. These slight in-plane displacements are very



III

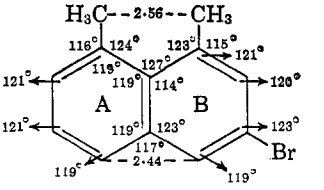


IV

effective in reducing the magnitude of interplanar twisting of the nitro group to only 49° as contrasted to 65° in nitromesitylene, 9-nitroanthracene, and 9,10-dinitroanthracene where in-plane deflections of the nitro group are difficult to realize (543). In 1-naphthoic acid too, the large in-plane deflection helps keep the angle of twist at 11°.

In 1,8-dinitronaphthalene (IV), one would anticipate even worse steric interactions. In an entirely planar model, the nonbonded O···O distance will be ~0.5 A as against the normal distance of 2.7 A. The serious interaction that would result from such an arrangement is avoided as follows: (i) the nitro groups are rotated about the C–N axis by 45° in one direction, (ii) the C–N bonds undergo a splaying apart to increase the N···N distance to 2.93 A from 2.42 A in a hypothetically planar model, (iii) the C–N bonds deviate from the aromatic plane by 0.37 A in opposite directions, and (iv) the carbon atoms bearing the nitro groups are also forced out of the plane of the molecule in the direction of the substituents resulting in slight nuclear distortion (9).

In view of what has been said concerning 1,8-dinitronaphthalene, a recent study (300) of 3-bromo-1,8-dimethylnaphthalene (V) is of interest. The various bond lengths observed in this molecule are not significantly different from those in similar environments (300). The *peri*-methyl groups are pushed apart by 0.42 A within the aromatic plane by an inplane bending (4°) of C–CH_3 bonds. This is reflected



V

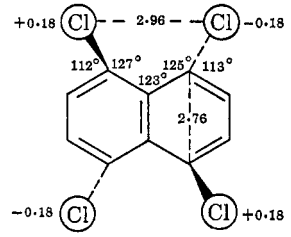
in the deformation of bond angles in the naphthalene portion of the molecule ($\angle C_8C_9C_1$ = 126.8°, $\angle C_4C_{10}C_5$ = 117.4°, $\angle C_{Me}C_1C_9$ = 122.9°, $\angle C_{Me}C_8C_9$ = 124.2°, $\angle C_4C_{10}C_5$ = 117.4°). A sizable increase in the nonbonded distance between the methyl groups to 2.56 A is seen in comparison with the $C_4\cdots C_5$ distance of 2.44 A. It is also seen that in ring A the bond angles do not show any large variation from those in naphthalene, while in ring B this change is considerable. This is attributed to a buckling of ring A which enables the bond angles in that ring to remain more or less unaffected. The presence of the heavy bromine atom in ring B is said to militate against any disturbance to planarity of the ring; this, however, introduces angle strain in the ring (300).

A number of workers (170, 196, 229, 447) have discussed the structure of octamethylnaphthalene, the only other *peri*-alkylnaphthalene derivative that has been studied so far. A brief reference to its conformation will be made later in this section.

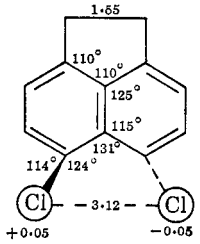
Several investigations have been made on *peri*-halonaphthalenes and the related haloacenaphthenes. Interest in these compounds stems from the fact that their halogens can be readily located through X-ray diffraction and that, at least in some cases, the steric effects can be discerned more clearly with substituents at least the size of the halogens (226). The compounds studied include 1,4,5,8-tetrachloronaphthalene (155–157, 228), 1,5-dichloro-4,8-dibromonaphthalene (157), 1,5-dibromo-4,8-diiodonaphthalene (157), octachloronaphthalene (229), 5,6-dichloroacenaphthene (27–29), and 5-chloro-6-bromoacenaphthene (29, 31). A few derivatives of naphthacenes which are formally related to *peri*-substituted naphthalenes have also been studied (8, 30, 32).

The structure of 1,4,5,8-tetrachloronaphthalene (VI) has been independently investigated by two groups, one in Russia (155–157) and the other in South Africa (228). Their experimental findings are in general agreement with each other. The mechanism for the relief of strain in this molecule is similar to that in 1,8-dinitronaphthalene. The observed bond lengths and bond angles in VI indicate that the steric strain is

spread out over the entire molecule, steeply falling off with increasing distance from the site of its origin. The β-hydrogen atoms restrict the in-plane bending of the *peri*-halogens. Therefore, the major escape from van der Waals strain is a propeller-like arrangement of the C–Cl bonds. Inasmuch as the carbon atoms carrying the halogens are also forced in



VI

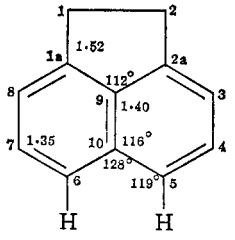


VII

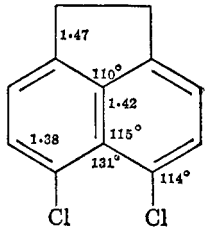
the direction of the displaced halogens, the nucleus assumes a chair-like conformation. As a result of nuclear distortions made possible by the elasticity of the naphthalene framework, the $C_1 \cdots C_4$ distance decreases to 2.76 A from the normal distance of 2.90 A in naphthalene.

A comparison of this molecule with the closely related 5,6-dichloroacenaphthene (VII) is interesting. In the latter, the presence of the dimethylene bridge across one set of *peri* positions pulls these carbon atoms together, causing a widening of the angle at the other end (399, 548). As a result, in 5,6-dichloroacenaphthene, there occurs a greater in-plane displacement of the halogens and only a small out-of-plane deviation (0.05 A as compared to 0.18 A in 1,4,5,8-tetrachloronaphthalene). Gafner and Herbstein (228) claim that the Cl···Cl distance (2.99 A) in the tetrahalo compounds is the shortest recorded between nonbonded chlorine atoms. In 5,6-dichloroacenaphthene this is increased to 3.12 A.

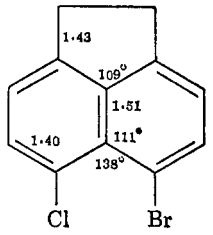
The bond angles and distances observed for acenaphthene (VIII) and its 5,6-dichloro- (IX) and 5-chloro-6-bromo- (X) derivatives provide an interesting comparison. There are noticeable changes in C_1–C_{1a} and C_9–C_{10} bond lengths. The former decreases steadily as one passes from VIII to X (VIII, 1.52 A; IX, 1.47 A; X, 1.43 A); the latter increases from VIII to X (VIII, 1.40 A; IX, 1.42 A; X, 1.51 A). A similar but less significant increase is noticed in the C_6–C_7 bond length. The changes in bond angles involving the carbon–halogen bonds are even more dramatic. The $C_5C_{10}C_6$ angle is widened systematically with the increasing bulk of the *peri* substituents. In these as well as several other sterically hindered compounds, carbon–halogen bonds seem to be generally longer than the normal C_{Ar}–halogen bonds. It is suggested that this is caused by a weakening of conjugation of the halogen atoms with the aromatic ring (29, 32, 227).



VIII

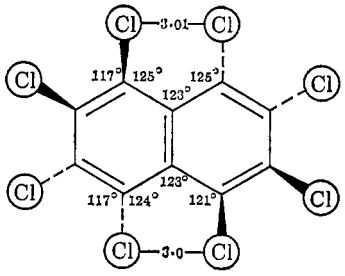


IX



X

A three-dimensional X-ray analysis of octachloronaphthalene (XI) has also been reported (229). Consistent with expectations, the molecule is severely deformed due to multiple displacements of the substituents and the nuclear carbon atoms. The α- and β-chlorine atoms are displaced out of plane by 0.54–0.79 and 0.37–0.47 A, respectively, and the out-of-plane displacement of each carbon atom is about one-third as much and in the same direction as its halogen substituent. As in the case of 1,4,5,8-tetrachloronaphthalene, this molecule also takes up a propeller-like conformation. The clearance between the nonbonded chlorine atoms is ~3.0 A. Evidence from Cl^{35} nuclear quadruple resonance of this compound has been recently presented, suggesting classification of the halogens in two groups (241).



XI

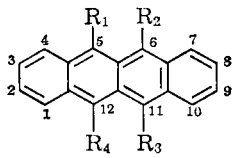
Deviations of the atoms from the mean molecular plane (in A)

C_1	−0.20	Cl_1	−0.60
C_2	−0.13	Cl_2	−0.40
C_3	+0.11	Cl_3	+0.40
C_4	+0.22	Cl_4	+0.75
C_5	−0.24	Cl_5	−0.79
C_6	−0.14	Cl_6	−0.37
C_7	+0.14	Cl_7	+0.47
C_8	+0.20	Cl_8	+0.54
C_9	−0.02		
C_{10}	+0.01		

In the light of above results, it is suggested (229) that the earlier findings of Donaldson and Robertson (170) regarding the molecular structure of octamethylnaphthalene are in need of revision. The latter workers suggested, on the basis of a two-dimensional X-ray analysis, that the α-methyl groups are displaced by 0.73 A from the mean plane corresponding to a 28° deviation of the C_{Ar}–CH_3 bond. The β-methyl groups also deviate by 0.25 A from planarity. Once out of plane, these bonds also undergo a slight outward displacement. Furthermore, adjoining methyl groups

move in opposite directions so that they are alternately above and below the general plane of the molecule. The experimental results also provide suggestive, but not conclusive evidence that the molecule undergoes slight nuclear distortions. A more elaborate solution of this problem must await further work on this molecule. There seems to be difficulty in obtaining crystals of suitable size to make possible a more precise crystal structure analysis (495). If the nuclear carbon atoms also move in the direction of the methyl groups, the trigonal sp^2 geometry at each carbon atom may be retained. Thus while the molecule as a whole is seriously distorted, the geometry around each nuclear carbon atom is planar. In molecules of this type, the situation is beautifully described as "the assembly of curved domes from planar tiles" (32).

Gafner and Herbstein (229) have discussed the steric strain and its relief in octachloro- and octamethylnaphthalenes. When the substituents alternate above and below the molecular plane, causing also nuclear distortions as outlined above, the substituent interaction energy will be minimized but the skeletal strain will be considerable. In a propeller-like conformation (*i.e.*, with two adjacent substituents up and the next two down, etc.) there is increased substituent interaction energy but less skeletal strain. The above authors believe that a double-chair conformation of the nucleus will be energetically preferable only when the bonding is tetrahedral as in cyclohexane; in overcrowded aromatic systems of the type discussed here, a propeller-like conformation is considered more likely. These views have also been examined in the case of a few naphthacene derivatives such as 5,6,11,12-tetraphenylnaphthacene (rubrene, XIIa), 5,6-dichloro-11,12-diphenylnaphthacene (XIIb), 5,11-dichloro-6,12-diphenylnaphthacene (XIIc), and 5,12-dichloro-6,11-diphenylnaphthacene (XIId) (8, 30, 32). In XIIa, XIIb,



XIIa, $R_1=R_2=R_3=R_4=Ph$
b, $R_1=R_2=Cl$; $R_3=R_4=Ph$
c, $R_1=R_3=Cl$; $R_2=R_4=Ph$
d, $R_1=R_4=Cl$; $R_2=R_3=Ph$

and 1,4,5,8-tetraphenylnaphthalene (255), even when the *peri*-phenyl substituents (which are tilted out of the main plane of the molecule) are parallel to each other in a plane perpendicular to the main plane, several unfavorably short nonbonded C···C distances occur (2.5 A as against 3.8 A needed to avoid steric repulsion). These interactions lead to molecular asymmetry, but the transformation of one stereoisomer to the other is considered difficult since it would involve surmounting a very high energy barrier for rotation of one phenyl group past the other phenyl (32). In XIIb, in-plane deflections of the chlorine atoms enabling them to get away from each other are limited by the buttressing action of the terminal phenyl groups at either ends. As a consequence, the chlorine atoms in the naphthacene derivative undergo an even larger (0.56 A) out-of-plane deflection than is the case with the chlorine atoms in 1,4,5,8-tetrachloronaphthalene (0.19 A) where only a weaker hydrogen-buttressing is possible. The C–C–Cl angles also indicate the same result. The phenyl substituents are twisted by 70° from the ring plane. Such an almost perpendicular orientation of *peri*-phenyl groups is also indicated by spectroscopic methods (281, 299).

Among a number of other polycyclic aromatic hydrocarbons that can be considered as *peri* derivatives of naphthalene, crystal-structure studies have been reported on benzo[*c*]phenanthrene (255, 265, 274, 276), 1,12-dimethylbenzo[*c*]phenanthrene (274–276), and tetrabenzonaphthalene (255, 266). A summary of the crystal structure analysis of these overcrowded molecules is available elsewhere (521).

B. MOLECULAR SPECTRA

1. *Ultraviolet Spectra*

The consequences of steric strain on the ultraviolet absorption spectra of polycyclic aromatic molecules have been well documented in the literature by several authors and notably by Jones (307, 309). Such studies have led to stimulating theoretical discussions. This section will present a summary of the observations made concerning the absorption characteristics of *peri*-substituted naphthalenes and a few other related derivatives.

The ultraviolet absorption spectrum of naphthalene itself consists of three absorption bands with λ_{max} at 312, 275, and 220 mμ, the respective ϵ_{max} values being 200, 5000, and 100,000. With the introduction of substituents, the band positions and intensities are modified depending upon the substituents. With di- and poly substituted naphthalenes the resulting spectra are even more complex and the spectral characteristics depend on whether or not the substituents enter into mutual conjugation through the aromatic ring and whether the systems are homo- or heteronuclear. When the substituents occupy positions susceptible to steric effects, this must also be considered in interpreting the spectral pattern. A careful comparison of spectral data on a large number of monosubstituted naphthalenes has revealed (55, 472) that with α substitution the 275-mμ band (^1L_a) is bathochromically shifted and superimposed on the weaker 312-mμ band (^1L_b), and with β substitution the middle band system is unaffected while the 312-mμ band is displaced to longer

wavelengths. The greater the conjugative interaction of the substituent is with the nucleus, the greater are the spectral changes. In disubstituted naphthalenes with groups capable of entering into conjugation with the naphthalene ring, in addition to the above three characteristic bands of naphthalene, an interaction or conjugation band appears at a longer wavelength (*e.g.*, at 400–440 mμ for nitronaphthylamines in ethanolic solution). The shape and intensity of this band seems to be a clear index of the electronic and steric effects operating in the molecule (55, 472). A few examples of such interactions will be discussed later in this section.

The manner in which steric effects influence the absorption bands of a molecule has been a matter of considerable discussion (217, 220). In naphthalene, the introduction of alkyl groups generally produces a bathochromic shift, leaving the general spectral pattern unaffected. Stronger interacting groups like amino, carboxyl, and nitro cause even larger bathochromic and hyperchromic changes. Overcrowding due to extensive substitution also results in considerable loss of fine structure. Several illustrations of this type are available (19, 50, 78, 161, 221, 269, 430) from studies on alkyl- and arylnaphthalenes. Dianov and Chernova (161) have found that a larger bathochromic shift occurs with 1,4,5,8-tetramethylnaphthalene than for the all β-substituted 2,3,6,7 isomer, particularly in the region 290–310 mμ. In 2,3,6-trimethyl-8-phenylnaphthalene, the appearance of fine structure around 320 mμ and an increased intensity are attributed to some, though weak, interaction of the α-phenyl substituent with the naphthalene system. In the more hindered systems in 2,3,6,8-tetramethyl-1-phenyl- and 2,3,6-trimethyl-1,8-diphenylnaphthalene, the loss of fine structure around 320 mμ is attributed to distortions within the molecule due to both out-of-plane rotation of the phenyl group and a widening between the C_{Ar}–Ph planes.

The spectra of polymethylnaphthalenes have also been recorded by Mosby (430), Abadir, Cook, and Gibson (1), and Heilbronner, Fröhlicher, and Plattner (263). Mosby has observed that in passing through the series 2,3,6,7-, 1,4,6,7-, 1,4,5,7-, and 1,4,5,8-tetramethylnaphthalenes, there is a progressive red shift (Table I). In the last compound, all the methyl groups occupy the α-naphthalene positions which possess greater conjugative interaction than the β positions, but the observed red shift may well be the result of overcrowding. This view seems to be supported by an even greater red shift for the decidedly nonplanar octamethylnaphthalene.

In the simpler phenylnaphthalenes (221, 249, 297) and binaphthyls (221), steric effects on spectra seem to be straightforward. Thus the case of isomeric 1- and 2-phenylnaphthalenes has become a classic example of steric inhibition of resonance. In the 1-phenyl isomer, lack of coplanarity and concomitant loss of conjugation

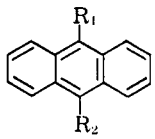
TABLE I

SPECTRA OF POLYMETHYLNAPHTHALENES (1, 263, 430)

Substituent	λ_{max}, mμ	ϵ_{max}
H	275	5000
1-Methyl	282	6300
2-Methyl	276	4800
2,6-Dimethyl	274	4700
2,7-Dimethyl	275	4900
2,3-Dimethyl	279	5100
1,8-Dimethyl	285	7100
1,5-Dimethyl	287	9100
1,4-Dimethyl	289	7600
1,3,8-Trimethyl	292	6300
1,4,5-Trimethyl	292	7900
2,3,6,7-Tetramethyl	270	4800
1,4,6,7-Tetramethyl	290	6600
1,4,5,7-Tetramethyl	292	7400
1,4,5,8-Tetramethyl	296	8300
1,2,3,4,5,6-Hexamethyl	298	7400
Heptamethyl	302	5000
Octamethyl	308	5000

lead to a spectrum essentially related to that of naphthalene, while that of 2-phenylnaphthalene indicates strong conjugation (221) and is very different from that of naphthalene. A similar steric effect presumably makes the spectra of 1,5-diphenylnaphthalene and 1-phenylnaphthalene alike (50).

A closer examination of the available data on phenylated polynuclear aromatics has provided interesting results. In the sterically hindered 9,10-diarylanthracenes (XIII), the spectra seem to be made up of

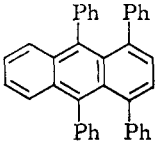


XIIIa, R_1 = Ph; R_2 = H
b, $R_1 = R_2$ = Ph
c, $R_1 = R_2$ = 1-naphthyl
d, R_1 = 9-anthryl; R_2 = H

the absorption of the component parts indicating almost total absence of electronic interaction between them in the ground and low-lying photoexcited states (162, 273, 308, 309). The similarity between the spectra of 9,10-dimethyl- and 9,10-diphenylanthracenes is presumably due to loss of conjugation in the latter.

The situation with *peri*-phenylated derivatives is not so clear in the naphthalene, anthracene, or naphthacene series. Dufraisse and Horclois (176) have found that the spectrum of 5,6,11,12-tetraphenylnaphthacene resembles that of the parent hydrocarbon which may be taken to suggest the lack of conjugation between the phenyls and the naphthacene system. Fuson and Tomboulian (225) have suggested from similar considerations that the 1,10-phenyl rings in 1,9,10-triphenylphenanthrene are parallel to each other in a plane that is perpendicular to the molecular plane. More recently, Douris (173) has investigated a few *peri*-phenylated naphthacenes and observed a bathochromic

shift with increasing phenyl substitution. This behavior may appear surprising since on conventional reasoning one would not expect such a bathochromic shift. Jaffé and Chalvet (299) have explained this behavior by postulating interactions between the π-electron systems even when they are perpendicular. Perhaps for a similar reason, bathochromic shifts are noted in the spectrum of 1,4,9,10-tetraphenylanthracene (XIV) (273) (Figure 1). Hirshberg has suggested (273) that the anthracene nucleus in XIV is so distorted that a limited amount of conjugation is rendered



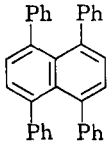
XIV

possible between the ring and phenyl substituents. A recent study (78) of some phenylnaphthalenes has indicated similar bathochromic shifts (Table II). For

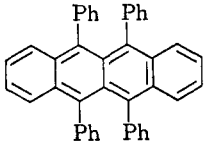
TABLE II
SPECTRA OF PHENYLNAPHTHALENES (78)

Substituent	λ_{max}, mμ	Log ϵ_{max}
H	275	3.80
2,7-Diphenyl	300	4.10
1,7-Diphenyl	302	4.05
1,3,6-Triphenyl	301	4.20
1,4,5,8-Tetraphenyl	334	4.18

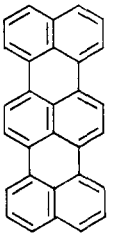
example, the spectrum of 1,4,5,8-tetraphenylnaphthalene (XV) is highly reminiscent of those of 1,4,9,10-tetraphenylanthracene (XIV) and rubrene (XVI), but entirely different from that of terylene (XVII)



XV



XVI



XVII

where the *peri*-phenyl systems are constrained to be coplanar. The above illustrations seem to indicate the general applicability of the concept of interactions between perpendicular π-electron systems. It is, however, not clear why such an interaction should not be invoked even with simple α- or *meso*-phenyl derivatives.

Substituted naphthalenes with simple unsaturated side chains (1-vinyl- and 1-propenylnaphthalene) show the effects of conjugation in their ultraviolet absorption spectra. When the olefinic bond is part of five- or six-membered ring (XVIII or XIX), there is inhibition of conjugation (327, 329) resulting from steric hindrance in the planar conformations. The presence of an 8-

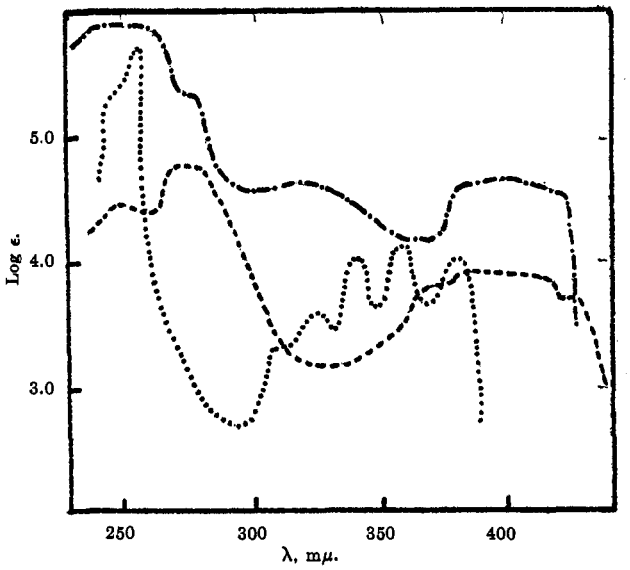
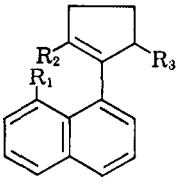
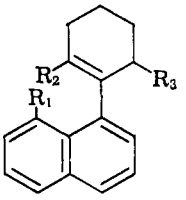


Figure 1. Reproduced from ref 273: anthracene, ...; 1,4,9,10-tetraphenylanthracene, - - - -; 1,4,5,8-tetraphenylanthracene, - · - · -.

alkyl substituent impedes whatever little residual conjugation there remains. Even when the ring size is



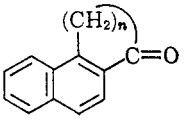
XVIIIa, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = Me$
c, $R_1 = Me$; $R_2 = R_3 = H$



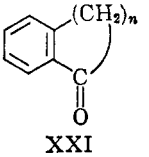
XIXa, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_2 = H$; $R_3 = Me$
c, $R_1 = Me$; $R_2 = R_3 = H$

enlarged to seven- or eight-membered ones, there does not seem to be any significant conjugation (331).

Huisgen and Reitz (284) have studied the absorption spectra of a number of cyclic ketones of types XX and XXI. The absorption band around 250 mμ in



XX



XXI

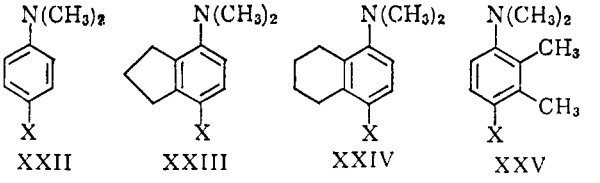
these compounds is believed to arise from carbonyl group conjugation with the ring. As one goes from $n = 5$ to $n = 8$, the intensity of this band is considerably decreased. This decrease in the naphthalene series is much more than that in the benzene analogs. This difference is attributed to the steric effect of *peri*-hydrogen in the former series. The spectra of the corresponding phenylhydrazones also support such a view (284).

We may now discuss the data obtained with other substituents. The absorption bands of 1-nitronaph-

thalene (λ_{max} 243, 342 mμ; log ϵ_{max} 4.02, 3.59 in ethanol) undergo a hypsochromic shift by the introduction of a 5-nitro (λ_{max} 233, 327 mμ; log ϵ_{max} 4.32, 3.81) or 8-nitro group (λ_{max} 231, 313 mμ; log ϵ_{max} 4.32, 3.81) (329). In the former, each of the nitro groups is presumed to counteract the conjugative ability of the other so as to make the electronic transition difficult; in the latter the observed effect is perhaps more steric than electronic in origin. Blyumenfeld (92) has also studied the absorption spectrum of 1,8-dinitronaphthalene and suggested that the molecule absorbs more as an aliphatic compound than a nitro aromatic compound.

A number of investigations have been directed to a study of the steric effects influencing the conjugation of an α-amino or dimethylamino group in naphthalene derivatives (24–26, 55, 411, 472). Pearson (472) has studied the spectra of nitro-1-naphthylamines in both ethanol and cyclohexane solutions. The data for the K bands of these compounds are listed in Table III. The low $\Delta\lambda$ (10 mμ) for 8-nitro-1-naphthylamine indicates that solvation of the excited molecule in the polar solvent leading to a stabilization of the excited state is not facile. The absorption intensities are also much lower for the *peri*-nitroamine. In nitro-2-naphthylamines, $\Delta\lambda$ values vary between 23 and 40 mμ.

A comparison of the K-band intensities of 4-nitro-1-naphthylamine (λ_{max} 434 mμ; ϵ_{max} 19,000) and 4-nitro-1-dimethylaminonaphthalene (λ_{max} 412 mμ; ϵ_{max} 9900) provides convincing proof of *peri* interactions. In the absence of steric effects, the change from $-NH_2$ to $-N(CH_3)_2$, if anything, should cause a stronger absorption as is the case with analogous benzene derivatives (*p*-nitroaniline, λ_{max} 378 mμ, ϵ_{max} 15,000; *p*-nitrodimethylaniline, λ_{max} 392 mμ, ϵ_{max} 20,000) (582). Similar data on a few other related derivatives presented in Table IV also illustrate this point. On the basis of these data the steric effect of an *o*-methyl group is suggested to be larger than that of *peri*-methylene in a six-membered ring which in turn is larger than that of *peri*-methylene in a five-membered ring. The same conclusion has also been arrived at by comparing the K-band intensities of XXII to XXV where X = $C_6H_5N{=}N-$, *p*-$O_2NC_6H_4N{=}N-$, $-CH{=}NOH$, and $-CN$. The intensities of the conjugation



bands steadily decrease as one passes from XXII to XXV (26).

Koptyug and Plakhov have determined the absorption spectra of *peri*-dihalonaphthalenes (353) and *peri*-halonaphthyl methyl sulfones (350). In going from 1,8-dichloronaphthalene to 1,8-chlorobromonaphthalene, a very distinct bathochromic displacement is observed in the 250–315-mμ region. The average shift is about 3 mμ. In the 1,7 isomers, the corresponding red shift is only 1 mμ. It is believed that steric strain in the molecule leads to a convergence of the energy levels of ground state and excited state (353). The fine structure of the long wavelength band decreases with increasing strain in the molecule. Thus the maximum observed at 323 mμ in 1,8-dichloronaphthalene is reduced to a weak inflection in 1,8-dibromonaphthalene. The absorption maxima around 328 mμ also show changes in band shape and intensity (Figures 2 and 3).

TABLE III

DATA ON THE K BANDS OF *x*-NITRO-1-NAPHTHYLAMINES (472)

Position of the nitro group	Ethanol λ_{max}, mμ	Ethanol Log ϵ_{max}	Cyclohexane λ_{max}, mμ	Cyclohexane Log ϵ_{max}	$\Delta\lambda$, mμ
2	428	3.95	404	3.87	24
3	416	3.43	382	3.54	34
4	430	4.25	377	4.07	53
5	416	3.34	385	3.43	31
6	412	3.35	385	3.47	27
7	436	3.62	401	3.65	35
8	400	3.21	390	3.30	10

TABLE IV

SPECTRAL DATA OF NITROAMINES[a] (25, 26)

Compound	λ_{max}, mμ	ϵ_{max}
4-Amino-7-nitrohydrindene	376	13,900
4-(N,N-Dimethylamino)-7-nitrohydrindene	387	12,600
5-Amino-8-nitrotetralin	383	11,400
5-(N,N-Dimethylamino)-8-nitrotetralin	364	5,700
Nitroaminodurene	395	15,700
5-Nitro-8-amino-6,7-dimethyltetralin	393	19,700
9-Nitro-10-amino-1,2,3,4,5,6,7,8-octahydroanthracene	397	22,400

[a] Only K bands are shown.

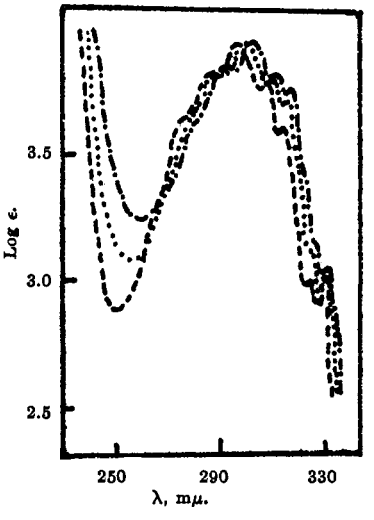


Figure 2.—Reproduced fron ref 353: 1,8-dichloronaphthalene, – – – –; 1-chloro-8-bromonaphthalene, ...; 1,8-dibromonaphthalene, - - - -.

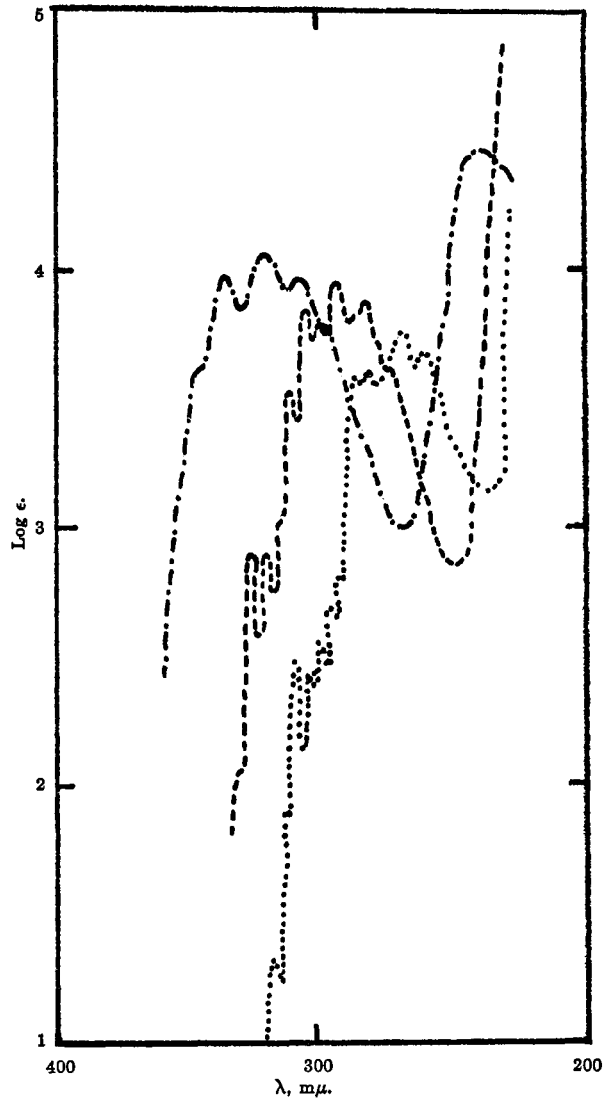
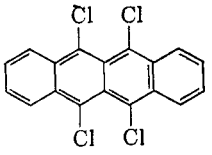


Figure 3.—Reproduced from ref 136: naphthalene, ...; 1,5-dichloronaphthalene, – – – –; 1,4,5,8-tetrachloronaphthalene, - - - - -.

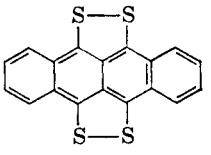
In view of the parallel spectral behavior observed with other sterically deformed systems like 4,5-dimethylphenanthrene and benzo[*c*]phenanthrene, the *peri*-halonaphthalenes should also be strained systems. Essentially similar spectral behavior is observed with methyl halonaphthyl sulfones also (350).

The views on 1,8-dimethylnaphthalene are conflicting. Oksengendler and Gendrikov (461) have not reported any special *peri* effects in this compound. Kalopissis (313) has, however, recorded a bathochromic shift of the ^1L_b band and attributed it to *peri* interaction. Koptyug and Plakhov (350) also believe that a *peri* effect is manifested in the spectrum of 1,8-dimethylnaphthalene but to a lesser magnitude than assumed by Kalopissis (313).

Clar and Marschalk (136) have studied a number of *peri*-halo and *peri*-sulfur derivatives of naphthalene, anthracene, and naphthacene. In all these cases, the ^1L_b and ^1L_a bands undergo bathochromic shifts. This shift is said to be additive for each halogen substituent in the outer rings, doubled for *meso* substitution, and greatly increased by *peri* substitution. These authors suggest that the *peri* effect is caused by the interpenetration of the electronic clouds of the *peri*-halogen or -sulfur atoms by virtue of their proximity. They even suggest a true conjugation between the π-electron systems of the *peri* substituents and attribute the deep color of such compounds (*e.g.*, XXVI and XXVII) to this type of conjugation. Koptyug and



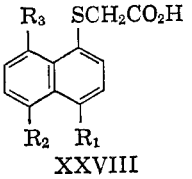
XXVI



XXVII

Plakhov (350), however, do not favor this view and prefer to consider it as a special case of *peri* interactions.

These ideas have been examined further (461) by analyzing the spectra of a number of 1-naphthylthioglycollic acid derivatives (XXVIII) with substituents at 4-, 5-, and 8-positions (Table V). In each series



XXVIII

the *peri* isomer is seen to have the maximum absorption at the longest wavelength. If $\Delta\lambda$ is taken to reflect the magnitude of the *peri* effect, this effect seems to be directly related to the nonbonded electron pairs available on the key atom of the *peri* substituent. Thus, the increasing order of the *peri* effect is suggested to be Br > Cl > OCH_3 > CO_2H. Any such *peri* effect is presumed to be absent in 1,4-, 1,5-, and 1,8-dimethylnaphthalenes in accordance with the above views.

The kinetics of oxidation of azonaphthalenes has provided a clear case of *peri* effects (47). Similarly,

TABLE V
ULTRAVIOLET ABSORPTION DATA OF 1-NAPHTHYLTHIOGLYCOLLIC ACIDS[a] (461)

Substituent	λ_{max}, mμ	ϵ_{max}	$\Delta\lambda$, mμ
None	303.0	6,500	...
8-CO_2H	303.0	5,500	0
5-OCH_3	307.5	9,800	4.5
4-OCH_3	308.0	9,600	5.0
8-OCH_3	313.5	10,700	10.5
5-Cl	312.5	7,300	9.5
4-Cl	315.0	8,200	12.0
8-Cl	327.0	8,400	24.0
5-Br	315.0	7,800	12.0
8-Br	327.0	7,900	24.0

[a] In ethanol.

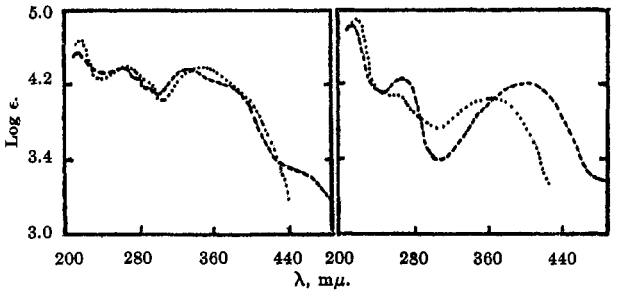


Figure 4.—Reproduced from ref 48: (left) 2,2′-azonaphthalene, – – – –; 2,2′-azoxynaphthalene, ...; (right) 1,1′-azonaphthalene, – – – –; 1,1′-azoxynaphthalene, ...

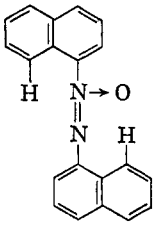
the spectral data of azo- and azoxynaphthalenes (48) also provide a strong case for the steric effects due to *peri* substituents. Aromatic azo compounds possess a strong conjugation band around 320–380 mμ in ethanolic solution. For the position of the K band in the following compounds, the order is azobenzene < azotoluene < 2,2′-azonaphthalene < 1,1′-azonaphthalene (Table VI). It is clear that the position of the

TABLE VI
K BANDS OF AZO AND AZOXY DERIVATIVES (48)[a]

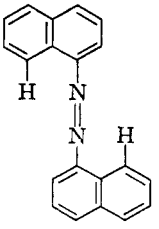
Compound	λ_{max}, mμ	Log ϵ_{max}
Azobenzene	318	4.32
o,o′-Azotoluene	332	4.24
2,2′-Azonaphthalene	335	4.37
1,1′-Azonaphthalene	400	4.21
Azoxybenzene	323	4.16
o,o′-Azoxytoluene	311	3.94
2,2′-Azoxynaphthalene	346	4.41
1,1′-Azoxynaphthalene	364	4.06

[a] In ethanol.

K band is shifted to longer wavelengths with increasing conjugation. The order is different with the corresponding azoxy compounds (Figure 4). In passing from azobenzene or 2,2′-azonaphthalene to the azoxy compound there is a bathochromic shift, while a similar change from *o,o′*-azotoluene or 1,1′-azonaphthalene to the azoxy compound causes a considerable blue shift. These observations would seem to indicate that steric effects are of importance in 1,1′-azoxynaphthalene (XXIX) but not in the azo compound XXX. Presumably, the overlap of the *peri*-hydrogen with azoxy oxygen is more than that between *peri*-hydrogen and azo nitrogen.

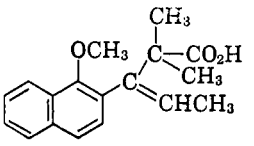


XXIX

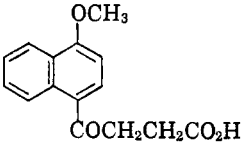


XXX

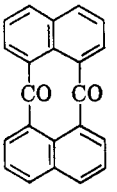
Instances are also on record showing inhibition to electronic interaction of 1-methoxyl (298) and 1-carbonyl groups with the naphthalene ring (243, 379) in derivatives like XXXI, XXXII, and XXXIII. It is interesting to note that the intensity of the band



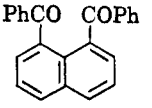
XXXI



XXXII



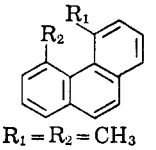
XXXIII



XXXIV

at 280 mμ is 9700 for XXXIV as against only 1100 for XXXII, clearly indicating a greatly weakened aryl–carbonyl interaction in XXXII (379).

In discussing the spectral features of *peri*-substituted naphthalenes, loss of fine structure of the absorption bands in the long wavelength region has been noticed in many cases. This effect has been noted in other polynuclear aromatic systems. In addition to references made earlier to such systems, several other studies may be mentioned on phenanthrenes (14, 46, 310, 431, 443, 476), benzo[*c*]phenanthrenes (49, 76, 303, 446), and chrysenes (220, 306). In 4,5-dimethylphenanthrene, for example, two groups of workers have independently reported (46, 443) the loss of the fine structure in the long wavelength region, even though the essential characteristics of phenanthroid absorption persisted. This is taken to indicate absence of nuclear distortion (as distinct from a mere out-of-plane bending of the methyl groups) in the molecule (46, 443). However, when the substituents are larger than methyl as in XXXV, fine structure is totally lost and the spectral pattern no longer conforms to that of phenanthrene (46). Essentially similar findings



XXXVa, $R_1 = R_2 = CH_3$
b, $R_1 = CHO$, $R_2 = CO_2CH_3$
c, $R_1 = R_2 = -CH_2-S-\overset{+}{C}(=NH)-NH_3Br$
d, $R_1 = R_2 = CH_2Br$

have been made on other such systems and further elaboration does not seem to be necessary.

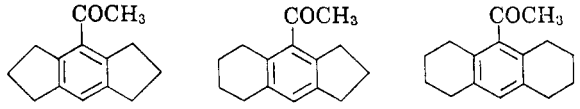
2. *Infrared Spectra*

Though a number of infrared studies have been reported concerning hydrogen bonding in appropriate naphthalene derivatives, some of which incidentally

throw light on *peri* effects (see section IIIC), only limited data are available on the infrared absorption of *peri*-substituted naphthalenes themselves. The only paper of this type is that of Topsom, Vaughan, and Wright (542). Earlier studies (132, 245, 261, 564, 585) were mainly directed to evolve some general correlations between C–H out-of-plane deformation frequencies and structure. Werner, Kennard, and Rayson (584) have examined a number of disubstituted naphthalenes and found that the bands due to three adjacent hydrogen atoms in 1,5 and 1,8 compounds occur in the region 770–795 and 810–825 cm^{-1}, respectively. Topsom, Vaughan, and Wright (542) have compared the absorption characteristics of 1,8-disubstituted naphthalenes with acenaphthene. In both cases, there are two groups of three adjacent hydrogens, and these compounds might be expected to show a single peak in the 600–900-cm^{-1} region. However, two absorption bands appear at 807–841 and 744–772 cm^{-1}. There is no agreement on the assignment of the origin of these two bands (245, 542, 584). No comments have been made about the existence of any special *peri* effects in these spectra. Perhaps such effects may become discernible from a study of the frequencies characteristic of the substituent groups rather than C–H deformation frequencies.

An interesting observation is made on the carbonyl stretching frequencies in XXXIV and XXXIII (379). The observed ν_{CO} for the twisted 1,8-naphthalylnaphthalene (XXXIII) is 25 cm^{-1} higher than in 1,8-dibenzoylnaphthalene.

An isolated example of Raman spectral measurements revealing *peri* effects in carbonyl compounds (22) is also presented here. In unhindered aromatic carbonyl compounds the Raman line occurs around 1690 cm^{-1} (*e.g.*, acetophenone, 1687 cm^{-1}), while in hindered-compounds it is pushed to higher frequencies around 1705 cm^{-1} (*e.g.*, acetomesitylene, 1707 cm^{-1}). Thus, in XXXVI, XXXVII, and XXXVIII, the carbonyl frequencies are observed at 1687, 1687, and 1708 cm^{-1}, respectively, substantiating the general conclusions that the *peri* interactions force the acetyl group out of the aromatic plane resulting in reduced conjugation of the carbonyl group with the aromatic ring. The magnitude of the steric effect is found to depend on the ring size.



XXXVI XXXVII XXXVIII

Katritzky and Ridgewell (317) have recorded the asymmetric (ν_{as}) and symmetric (ν_s) vibrational frequencies of the nitro group in 1- and 2-nitronaphthalenes. The ν_{as} values are at 1528 and 1532 cm^{-1} and ν_s at 1340 and 1352 cm^{-1}, respectively. The intensity of ν_s in the 1-nitro compound is 280 while that for the 2 isomer is 550. The order is, however, reversed for the intensities of ν_{as} (420 for the 1 isomer and 280 for the 2 isomer). It is not clear if the intensity variations are a consequence of *peri* effects in the 1 isomer. These authors have also studied ν_{OMe} for 1- and 2-methoxynaphthalenes. In the 1-methoxy compound, ν_{OMe} occurs at 1104 cm^{-1} and in the 2 isomer at 1033 cm^{-1}. The absorption frequency in the 2-methoxy compound corresponds to those in unhindered methoxy derivatives (1013–1048 cm^{-1} in monocyclic aromatic methoxy derivatives and 1024–1040 cm^{-1} in bicyclic derivatives). The shift of this absorption to higher frequencies in the 1 isomer is attributed to strong steric effects (317) and is comparable to those observed in 2,6- and 2,3-substituted anisoles which also lack absorption in the 1020–1040-cm^{-1} region.

Elliott and Mason (185) and Krueger (356) have studied the N–H stretching frequencies and intensities of hindered and unhindered polycyclic aromatic amines. Elliott and Mason (185) determined the position and intensity of ν_{as} of the N–H stretching vibration bands in the 3400-cm^{-1} region for a series of such amines. Table VII contains some of their data concerning $\nu_{N-H(as)}$ and the estimated HNH angles (θ) in these amines. It is seen that the aforementioned frequencies are pushed slightly, but consistently, to lower frequencies in the *peri* amines except in the case of 3-aminopyrene and 9-anthrylamine. However, in all the *peri* and *meso* amines, θ decreases from 111.1 to 112.7° observed in the unhindered amines to 109.4–110.8°. The value of θ is at a minimum (107.1°) in cyclohexylamine. In *peri* amines, the reduction of θ from the aniline value is considered to arise partly from inhibition of nitrogen lone-pair resonance with the aromatic ring and partly

TABLE VII
INFRARED N–H FREQUENCIES AND HNH ANGLES (θ) IN POLYCYCLIC AMINES (185, 356)

Compound	ν_{as}, cm^{-1}	θ, deg
Aniline	3473	111.1
m-Aminobiphenyl	3476	111.9
p-Aminobiphenyl	3480	112.1
2-Aminofluorene	3475	111.9
2-Naphthylamine	3477	111.6
3-Phenanthrylamine	3480	112.4
2-Anthrylamine	3480	112.7
1-Naphthylamine	3470	110.3
1-Phenanthrylamine	3471	110.0
9-Phenanthrylamine	3464	109.8
1-Anthrylamine	3468	110.6
2-Aminochrysene	3469	110.1
3-Aminopyrene	3482	110.8
9-Anthrylamine	3489	109.4
Cyclohexylamine	3375	107.1
1-Amino-2-nitronaphthalene	3522	132.8
2-Amino-1-nitronaphthalene	3514	122.3
2-Amino-3-nitronaphthalene	3515	117.7
1-Amino-8-nitronaphthalene	3456	118.5

from direct compression of this angle. That there is in all these cases some sp^2 character to the N–H bonds in aromatic amines is shown by the higher values of θ in them as compared to that in cyclohexylamine. The variations noticed in antisymmetric N–H stretching vibrations and intensities are also attributed to steric effects (185) in *peri* amines. The exceptional behavior of 3-aminopyrene noticed here has been also pointed out in another investigation (199).

Krueger (356) has estimated the values of θ and N–H stretching force constants for a number of substituted 1- and 2-naphthylamines from the data of Bryson (112). His data also indicate two distinct correlations between the s character of nitrogen bonding orbitals and the force constants depending upon the position of the amino substituent. It is appropriate to consider both the s character of nitrogen bonding orbitals and the charge density on the amino nitrogen atom in discussing variations in N–H stretching force constants. Changes in θ are said to be solely governed by the nature of the nitrogen bonding orbitals. The larger values of θ in *ortho*- and *peri*-substituted nitronaphthylamines (Table VII) are presumed to arise from intramolecular hydrogen bonding.

3. *Nuclear Magnetic Resonance Spectra*

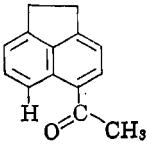
During the last decade, nuclear magnetic resonance (nmr) spectroscopy has become increasingly popular with the structural organic chemist. In line with this trend, the molecular interactions in *peri*-substituted naphthalenes and related derivatives have also been studied through nmr methods. Naphthalene itself is found to present a spectrum with the α-proton resonance at τ 2.20 and the β-proton resonance at τ 2.56 (231). The presence of other substituents in the naphthalene nucleus affects the resonance positions of the remaining protons.

In naphthalene-1-sulfonic acid, the resonance signals of the *ortho* and *para* protons are shifted to considerably lower fields, whereas the *meta* and *peri* protons are affected to a lesser extent. The displacement of the *peri* proton is only −0.15 ppm which, however, is at a higher field than the *meta* and heteronuclear protons. This could well be due to electrical field effects and magnetic anisotropy effects from the adjacent sulfonic acid group (231).

Several authors have observed a significant deshielding which appears to result from *peri* effects (174, 577, 579). In 1-nitronaphthalene, the chemical shift of the *peri* proton is τ 1.64 compared to τ 2.20 in naphthalene itself for the α proton. That this deshielding is due to the nitro group is shown by examining the effect of introducing a methyl group *ortho* to the nitro group. In 1-nitro-2-methylnaphthalene, the chemical shift of the *peri* proton is τ 2.32 as against a calculated value of τ 1.69. This reversal of the chemical shift of the *peri* proton in going from 1-nitronaphthalene to the 2-methyl derivative is attributed to the nonplanar twisting of the 1-nitro group. For the same reason, the proton chemical shifts of H_3 and H_4 in 1-nitro-2-methylnaphthalene are also found to be at higher fields by τ 0.10 and 0.16, respectively. Supporting data have been obtained from measurements on 2,3-, 2,6-, and 2,7-dimethyl-1-nitronaphthalenes (577, 579). The data on nitromethylnaphthalenes further reveal that the aliphatic proton signals are also affected by the presence of a nitro group but to a relatively much smaller degree than in the case of the ring protons. The largest shift of −0.21 ppm occurs in 3-methyl-2-nitronaphthalenes, equaling that of the *o*-methyl group in 2,5-dimethylnitrobenzene. The methyl proton shift is almost negligible in 1-nitro-2-methylnaphthalene where the nitro group is twisted out of the molecular plane. In 8-methyl-1-nitronaphthalene, the shift is found to be upfield by 0.15 ppm and is attributed to magnetic anisotropy variations of the 1-nitro group (577).

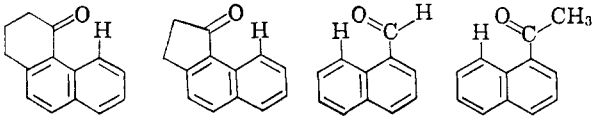
Wells (576) has measured the proton resonance shifts in a number of dinitronaphthalenes. The *ortho*-proton shifts are of the order 2α (−1.06) > 1β (−0.77) > 3β (−0.67). The values observed for the nonadjacent protons are in the range −0.23 to −0.29 ppm except for the *para* (4α, −0.46 ppm), *peri* (8α, −0.47 ppm), and 7α (−0.49 ppm) interactions. While the *peri*-proton interaction is attributable to a unique spatial arrangement, the 7α interaction is believed to be due to the presence of the proton on the same side of the aromatic ring as the oxygen atom of the nitro group.

Dudek (174) has investigated the nmr spectra of several 1-substituted naphthalenes and found that in all cases, the *peri* proton is considerably deshielded by the adjacent α substituent. This is particularly true of OH, OCH_3, and NH_2 groups as α substituents. In these cases, the *peri* hydrogen prefers the *trans* arrangement of the 8-substituent. Under these conditions, the *peri* hydrogen would be within 2.40 A from the lone-pair electrons on the adjacent oxygen or nitrogen. If this could be construed *as a type of* hydrogen bond (the normal distance for hydrogen bond is 2.70 A), the downfield shift of the *peri* proton could be readily explained. This shift is about 0.5 ppm and is significantly higher than the usual aromatic proton shifts (~0.2 ppm) attributed to solute–solvent hydrogen bonding. The poor acceptor ability of the aromatic hydrogen is suggested to have been compensated for by the extra proximity of the *peri* positions by virtue of their fixed geometry. Dudek has also discussed the



conformation of 5-acetylacenaphthene from nmr data and favors the $H_6\cdots$acetyl methyl *trans* arrangement.

The deshielding of the *peri* protons in 1-formyl-, 1-acetyl-, and 1-carbethoxynaphthalenes has also been studied (404). The deshielding is found to decrease with the increasing bulk of the α substituent. When



−100 cps −76 cps −75 cps −52 cps

the carbonyl group is locked *trans* to the *peri* proton as in 2-hydroxy-1-formylnaphthalene (owing to hydrogen bonding), the downfield displacement of the *peri*-proton signal is much less (−33 cps). This is restored to −94 cps in 2-methoxy-1-formylnaphthalene (absence of hydrogen bonding). Similar *peri* effects are also observable in partially saturated naphthalene derivatives. For example, in 2-methoxy-5,6,7,8-tetrahydronaphthalene, the H_4 signal appears at τ 3.04. In 2-methoxy-5-methyl-5,6,7,8-tetrahydronaphthalene, H_4 proton absorption occurs at τ 2.88, thus undergoing a deshielding of τ 0.16 by the adjoining methyl substituent (436). The aromatic and aliphatic proton spectra have been examined for many dimethylnaphthalenes (397, 435). Generally, the magnetic shielding of the proton (both α and β) increases in the dimethyl derivatives compared to naphthalene. In 1,4- and 1,5-dimethylnaphthalenes, the α protons are hindered sterically by the adjoining *peri*-methyl groups which cause a deshielding of these protons. A variation in the methyl proton shifts is also noticeable. The downfield shifts observed in 1,8-dimethylnaphthalene as compared to other isomers is considered to reflect the steric strain in this molecule (397) (Table VIII). From another investigation (435) on polymethyl- (and other alkyl-) naphthalenes, the following generalizations are suggested: (a) an α-methyl group is deshielded more than a β-methyl group; (b) an alkyl group *ortho* to methyl causes a shielding of 4 cps, with *meta* orientation it is about 2 cps, and with *peri* orientation it is at a maximum (12 cps).

The recent studies on the nmr spectra of polyphenylnaphthalenes (53, 281, 483a) and anthracenes (162) are of much interest. The phenyl protons in 1,8-diphenylnaphthalene absorb at τ 3.15 and are upfield relative to those in 1-phenylnaphthalene (τ 2.62) and 1,7-diphenylnaphthalene (τ 2.51) (281). This upfield shift in the *peri* derivative is comparable to that observed in the pair *p*-xylene (τ 2.95) and paracyclophane (τ 3.63) and presumably results from mutual shielding of the phenyl protons facilitated by the parallel orientation of the phenyl rings. In 1,4,5,8-tetraphenylnaphthalene, the proton signals appear at τ 2.80 (singlet, 4 H), 3.00 (triplet, 4H), and 3.23 (doublet, 16 H). The singlet is attributed to the naphthalene β protons, the triplet to the *para* protons of the phenyl rings, and the doublet to the *ortho* and *meta* protons of the phenyl rings. The upfield shift of the doublet is attributed to interaction between the parallel π-electron systems. The nonequivalence of the *p*-phenyl protons with the other phenyl protons is said to result from the spatial disposition of the phenyl groups in 1,4,5,8-tetraphenylnaphthalene in which the *peri*-phenyl groups are not quite parallel (in contrast to the parallel arrangement of the phenyl groups in 1,8-diphenylnaphthalene where all the phenyl protons are found to be equivalent) but slightly bent outwards (483a). A similar observation is reported from a study of the nmr spectra of 1,9-diphenyl-, 1,9,10-triphenyl-, and 1,4,9,10-tetraphenylanthracenes. In these compounds the phenyl protons absorb around τ 3.0, while in 1,10-diphenylanthracene (with no parallel π-electron systems) the corresponding signal is observed at τ 2.43 (162).

Polynuclear systems other than naphthalene have also attracted attention in recent years and a vast amount of nmr data on these derivatives are available. In several instances, *peri* effects are found to be significant. These studies include data on phenanthrenes (403, 404, 408, 436, 479, 485), benzo[*c*]phenanthrenes (402, 408, 450), biphenylenes (405), pyrenes (402, 407), and heteropolycyclic compounds (406, 497, 522).

TABLE VIII
CHEMICAL SHIFTS IN DIMETHYLNAPHTHALENES (397)

Compound	Chemical shift (cps relative to water as external reference)	
Dimethylnaphthalene	Ring α protons	Aliphatic protons
(Naphthalene)	−117.0	...
2,3-	−105.0	+99.3
2,6-	−104.6	+94.1
2,7-	−100.8	+94.8
1,4-	−121.0	+88.7
1,5-	−115.2	+86.7
1, 8-	...	+78.7

C. DIELECTRIC MEASUREMENTS

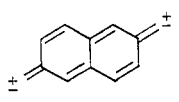
The application of dielectric measurements as a tool for the determination of configuration and conformation of organic molecules is well established. The approach is based on the experimental determination of the dipole moment, the molar Kerr constant (or the dielectric relaxation time) of the molecule under study, followed by comparison with data calculated for suitable theoretical models. In choosing these models, one must consider the possible steric and polar factors too. The structure for which there is closest agreement between the calculated and the observed values is likely to represent the actual structure of the molecule. A number of such studies have been made on naphthalene derivatives with particular interest directed to investigating *peri* interaction of substituents.

Another approach is the study of solvent effects on these properties. For example, when the dipole mo-

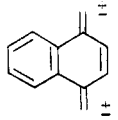
ment of a compound is determined in a nonpolar solvent, such as benzene (μ_b), and a polar solvent, such as dioxane (μ_d), the difference in the dipole moment ($\Delta\mu$) often provides useful clues regarding the structure of the solvated molecule. The utility of these methods is documented in a number of textbooks, monographs, and reviews.

1. *Electric Dipole Moments*

For monosubstituted naphthalenes, the moment of the 2 isomer is generally greater than that of the 1 isomer, irrespective of the type of substituent. This is explained as being partly due to a longer conjugated system (XXXIX) in the 2 isomers than in the 1 isomers (XL) and partly to a possible twisting (in-plane and/or out-of-plane) of the 1-substituent that would lead to a

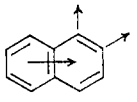


XXXIX

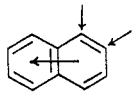


XL

reduction of conjugation of the substituent with the naphthalene system (55, 395, 492). It has also been observed that the moments of 1-naphthyl compounds are quite close to those of the corresponding benzene derivatives. It has been suggested (492) that this coincidence indicates that any steric effect caused by *peri*-hydrogen is just counterbalanced by the dielectric contribution from the other ring in the naphthalene derivative (XLI and XLII).



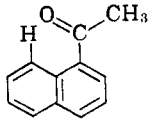
XLI
(-M substitution, *e.g.* $-NO_2$, $-COCH_3$)



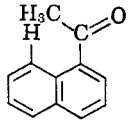
XLII
(+M substitution, *e.g.* $-NH_2$, $-OCH_3$)

Lutskii and Kochergina (395) have carefully analyzed the differences ($\Delta\mu_{\beta-\alpha}$) between the moments of 1- and 2-naphthyl derivatives (μ_α and μ_β, respectively) and the corresponding benzene derivatives. Judged from the magnitude of $\Delta\mu_{\beta-\alpha}$, the steric effect due to *peri*-hydrogen is believed to affect the conjugation of bulky groups like $-NO_2$, $-COCH_3$, and $-CO_2R$ with the 1-position of naphthalene.

A more thorough examination of some of these compounds has been made recently (55). The observed dipole moment of 1-acetylnaphthalene is 2.89 D. in benzene at 30°. The molecule may exist in two planar conformations XLIII and XLIV in both of which

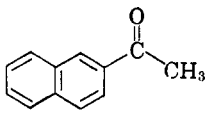


XLIII

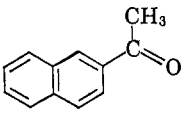


XLIV

there will be considerable overlap of *peri*-hydrogen with the carbonyl oxygen (XLIII) or methyl (XLIV) of the acetyl group. The moments calculated for these conformations are 2.67 (XLIII) and 3.30 D. (XLIV), respectively. Neither of them corresponds to the experimental value (2.89 D.). The observed value is, however, closer to that of XLIII. One reason for this preference may be (56) the *trans* disposition of the double bonds (C=O and C_1=C_2) in XLIII, since some fixation of double bonds in naphthalene is now admitted (210). For an identical reason, conformation XLVI (μ_{calcd} = 2.98 D.) is preferred to XLV (μ_{calcd} = 2.85 D.) for 2-acetylnaphthalene (μ_{obsd} = 3.08 D.) (55);



XLV



XLVI

free rotation of the 2-acetyl group would favor both conformations equally. The observed moment of the 1-acetyl compound may be explained even better by considering a slight nonplanar variation derived from XLIII.

The existence of *peri*-methine hindrance is made more evident from an inspection of the dipole moments of some amines presented in Table IX. On passing from

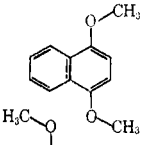
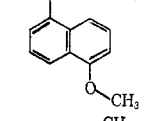
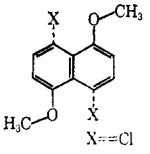
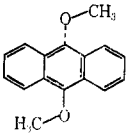
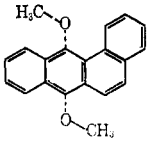
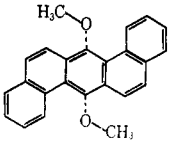
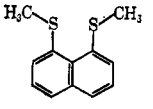
TABLE IX
ELECTRIC DIPOLE MOMENTS OF SOME AMINES

Compound	μ_{obsd}, D.	Difference	Ref
Aniline	1.53		55
Dimethylaniline	1.61	+0.08	55
2-Naphthylamine	1.71		55
2-Dimethylaminonaphthalene	1.90	+0.19	55
o-Toluidine	1.59		519
Dimethylamino-*o*-toluidine	0.96	−0.63	519
1-Naphthylamine	1.50		519
1-Dimethylaminonaphthalene	1.06	−0.42	519

aniline to dimethylaniline, there is a slight increase (0.08 D.) in dipole moment. The same trend is observed in the pair 2-naphthylamine and 2-dimethylaminonaphthalene (0.19 D.). This is in marked contrast to the considerable decrease in moment as one goes from *o*-toluidine or 1-naphthylamine to the dimethylamino compound. The decrease is obviously due to a strong suppression of the mesomeric effect of the dimethylamino group in the hindered amines. The case of 4-nitro-1-dimethylaminonaphthalene is also similar. The mesomeric interaction between $-NO_2$ and $-N(CH_3)_2$ is severely retarded as reflected in the low interaction moment (0.54 D.) observed for this compound (55). The interaction moment observed for the unhindered *p*-nitro-N,N-dimethylaniline is 1.48 D.

Several other examples of *peri* interactions may be found among disubstituted naphthalenes. The observed dipole moment of 1,8-dichloronaphthalene is 2.88 D. (575) and of 1,8-dinitronaphthalene is 7.1 D.

TABLE X
ELECTRIC DIPOLE MOMENTS AND CONFORMATIONS OF SOME NAPHTHALENE AND ANTHRACENE DERIVATIVES

Compound	Preferred conformations	Description of the conformations	μ_{obsd}, D.	Ref
1,4-Dimethoxynaphthalene		Planar *cis*, libration of OCH_3 possible	1.73	188
1,5-Dimethoxynaphthalene		Planar *trans*, libration of OCH_3 possible	0.67	188
4,8-Dichloro-1,5-dimethoxynaphthalene	 X=Cl	Nonplanar, tilting of the substituents and some of the nuclear carbon atoms above and below the mean plane (see text)	0.95	188
4,8-Dibromo-1,5-dimethoxynaphthalene	As above X=Br	As above	0.93	188
9,10-Dimethoxyanthracene		OCH_3 nearly orthogonal to the ring plane	1.73	189
9,10-Dimethoxy-1,2-benzanthracene		As above	1.65	189
9,10-Dimethoxy-1,2,5,6-dibenzanthracene		As above	1.67	189
1,4-Bis(methylthio)naphthalene		Planar *cis*	1.93	389, 390
1,5-Bis(methylthio)naphthalene		Planar *trans*	1.28	389, 390
1,8-Bis(methylthio)naphthalene		SCH_3 rotated 40° out-of-plane	1.82	389, 390

(437). These are considerably lower than the calculated moments, assuming that the molecules are planar and that the dipole vectors act along the *peri*-bond axes (μ_{calcd} for 1,8-$C_{10}H_6Cl_2$, 3.18 D.; for 1,8-$C_{10}H_6(NO_2)_2$, ~8.0 D.). This discrepancy is attributed to a deflection of the bonds carrying these substituents. Such a deflection has also been inferred from X-ray studies on 1,8-dinitronaphthalene (9). Nakata (437) has suggested an angle of 50° between C_{Ar}–NO_2 bonds. In support of this, de Laszlo (362) points out a similar spreading out of the C_{Ar}–halogen bonds in 1,8-diiodonaphthalene from electron-diffraction studies.

An interesting series of investigations on methoxynaphthalenes and methoxyanthracenes (188, 189, 388) and 1,4- 1,5-, and 1,8-bis(methylthio)naphthalenes (389, 390) are available. Table X is a summary of these results. In all these cases, the *peri* substituents orient themselves in such a way as to avoid steric interaction between contiguous groups. The free rotation of the dipole vectors is limited by restrictions imposed by resonance interactions with the ring and the steric bulk of the *peri* substituent. The conformations which are most consistent with the observed dipole moments are also indicated in Table X. It is noteworthy to observe that π bonding between sulfur and the ring in the methylthio compounds is less effective than that between oxygen and the ring in the methoxy compounds, as revealed by the larger torsional oscillations noted for the sulfur derivatives.

A few more observations on the data of Table X appear worthwhile. An out-of-plane movement of the *peri* substituents is postulated in 4,8-dichloro- and 4,8-

dibromo-1,5-dimethoxynaphthalene (188) and 1,8-bis-(methylthio)naphthalene (389). In the halo compounds the out-of-plane deviation is about 18° and the in-plane deviation is about half as much. The substituents are also said to be alternately displaced upward and downward with the nuclear carbon atoms nearest to them being similarly deflected by 9° (188). As a result, the conformation of the molecule is very similar to that of 1,4,5,8-tetrachloronaphthalene determined by crystal-structure methods (156, 157, 228). In 1,8-bis(methylthio)naphthalene, the methylthio groups are forced 40° out-of-plane so that the sulfur atoms are separated by about 3.7 A. An apparently simple and more desirable compound to study molecular conformations of this type through dipole moments would be 4,8-dibromo-1,5-dimethylnaphthalene in which there are no complications associated with a rotating vector like $-OCH_3$ or $-SCH_3$, but this compound has proved too difficult to synthesize (535).

Several other examples of preferred conformations have been investigated among acetylnaphthols (393) and their methyl ethers (55, 393), nitronaphthols (393) and their methyl ethers (55, 393), and hydroxynaphthoic acids and their derivatives (394, 396). In each series, the conclusions are essentially the same as those explained by the foregoing illustrations, unmistakably suggesting the steric effect of *peri* substituent.

As indicated earlier, solvent-effect studies on dipole moments to examine the *peri* effect have been made. Richards and Walker have determined the dipole moments of nitrophenols and nitronaphthols (490) as well as nitroamines (491). Their data pertinent to our present discussion are given in Table XI. The presence of *p*-nitro group is seen to cause a large positive difference in dipole moment on passing from benzene to dioxane as solvent. If this behavior is related to the mesomeric withdrawal of electrons by the *p*-nitro substituent from the interaction site, the smaller effect of the 4-nitro group in entry 6 in Table XI should be at least in part due to its nonplanarity with the nucleus. On the other hand, the unhindered *p*-nitro group in the benzene series (entries 2 and 4) exerts its maximum electron-withdrawing effect. This, however, is not likely to be the sole reason for this difference because the mesomeric effect of the substituents also differs with the nature of the aromatic ring to which it is attached (490).

TABLE XI (490)
ELECTRIC DIPOLE MOMENTS OF SOME PHENOLS AND NAPHTHOLS

No.	Compound	μ_B, D.	μ_D, D.	$\Delta\mu$, D.
1	*o*-Nitrophenol	3.22	3.07	−0.15
2	2,4-Dinitrophenol	3.02	3.51	+0.49
3	2,6-Dinitrophenol	3.89	3.47	−0.42
4	2,4,6-Trinitrophenol	1.51	2.13	+0.62
5	2-Nitro-1-naphthol	3.79	3.62	−0.17
6	2,4-Dinitro-1-naphthol	4.19	4.40	+0.21
7	1-Nitro-2-naphthol	3.68	3.79	+0.11

The $\Delta\mu$ value of 2-nitro-1-naphthol is negative (−0.17 D.), whereas that for 1-nitro-2-naphthol is positive (+0.11 D.). This is said to indicate absence of dipolar association between dioxane and the 1-nitro group, the latter being shielded by the *peri*-hydrogen (490). Probably for a similar reason, there does not seem to be any significant solute–solvent interaction between 2-nitro-1-naphthylamine and dioxane. In 8-nitro-1-naphthylamine also, the dipole moment data give no evidence of inter- or intramolecular association in carbon tetrachloride or dioxane solutions (491) (see, however, the section on infrared spectra).

2. *Molar Kerr Constants*

Attempts to correlate the conformation of substituted naphthalenes (366, 368), decalins (179), binaphthyls (367), 1,3,5-tri(naphthyl)benzenes (367), and anthracenes (368) by determining their molar Kerr constants are also on record. Monosubstituted naphthalenes which have been discussed (366) include the methyl-, hydroxy-, methoxy-, formyl-, acetyl-, cyano-, nitro-, and aminonaphthalenes. All the substituents except OH and CN seem to be sterically affected by the *peri*-hydrogen. Table XII lists the data on these and other related compounds. The results obtained on the methoxynaphthalenes and methoxyanthracenes are in general harmony with the conclusions of Everard and Sutton (188, 189) from dipole moment studies. The nonplanarity indicated for 1,1′-binaphthyl ($\theta = 48°$) is consistent with its reported optical activity (258), crystal structure (106), and absorption spectrum (221). A nonplanarity with $\theta = 26°$ is suggested for the 1-naphthyl groups in 1,3,5-tri(1′-naphthyl)benzene. In this connection, it is interesting to note that crystal structure measurements (10) of hexaphenylbenzene reveal an almost orthogonal arrangement of the peripheral rings with an oscillation of ±10° about the Ph–C bonds. It has, however, been pointed out (367) that the interplanar angles arrived at from Kerr constant studies should not be compared with values obtained from measurements on the crystalline or gaseous state. For example, crystal studies (106) indicate an interplanar angle of 73° in 1,1′-binaphthyl, whereas Kerr constant measurements (367) would suggest only 48° for this.

3. *Dielectric Relaxation*

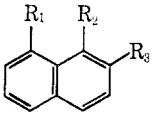
The dielectric relaxation times (216, 246, 493) of several monosubstituted naphthalenes have been determined. It is generally observed that hindrance to free rotation of an α substituent causes an increase in the relaxation time. Thus the relaxation times (in decalin at 20°, 10^{-11} sec) for some of these compounds are as follows: 1-methoxy, 55.2; 2-methoxy, 33.1; 1-ethoxy, 105.0; 2-ethoxy, 56.2. The relaxation times for 1-substituted naphthalenes themselves increase with

TABLE XII
MOLAR KERR CONSTANTS AND CONFORMATION

Compound	Molar Kerr constant × 10^{12} Obsd[a]	Molar Kerr constant × 10^{12} Calcd[b]	Interplanar angle (θ), deg	Ref
1-Methylnaphthalene	51.4	58.7	...[c]	366
1-Methoxynaphthalene	151.0	154.0	19 (*trans*)	366
1-Formylnaphthalene	554.5	539.0	15 (C=O and *peri*-H *trans*)	366
1-Acetylnaphthalene	341.0	345.0	30 (C-methyl and *peri*-H *trans*)	366
1-Nitronaphthalene	970.4	1576.0	...[c]	366
1-Aminonaphthalene	81.1	82.8	28	366
1,4-Dimethoxynaphthalene	298.3	286.0	±30	368
1,5-Dimethoxynaphthalene	41.0	56.3	...[c]	368
1,1′-Binaphthyl	145.6	144.4	48	367
2,2′-Binaphthyl	340.5	344.0	0	367
1,3,5-Tri(1′-naphthyl)benzene	370.0	366.8	26	367
9-Methoxyanthracene	34.3	33.1	30	368
9,10-Dimethoxyanthracene	−189.0	−200.0	±75	368

[a] In CCl_4, 25°. [b] For the most probable conformation. [c] Not specified.

TABLE XIII
RACEMIZATION OF OPTICALLY ACTIVE *peri*-NAPHTHALENES

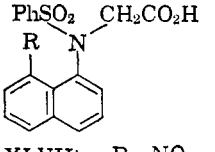


R_1	R_2	R_3	$t_{1/2}$, min	Solvent	Temp, °C	Ref
$-N(COCH_3)(alkyl)$	SO_3H	H				425
$-N(SO_2Ph)(CH_2CH_2OH)$	NO_2	H	27	$CHCl_3$	25	238
CO_2H	*o*-$(CH_3)_3CC_6H_4$–	H				372
CO_2H	SOPh	H				503
H	$-CCl=CRCO_2H$	CH_3	4200 (R = Me)	BuOH	Bp of solvent	4
	R = H or Me		70 (R = H)	BuOH	Bp of solvent	
H	4,6-Dinitro-2-carboxy	H				371
H	*o*-$HO_2C \cdot C_6H_4$–	H	2	$CHCl_3$	20	249
CO_2H	*o*-$HO_2C \cdot C_6H_4$–	H	230 ± 40	$CHCl_3$	20	249

the size of the substituents (benzene, 20°, 10^{-11} sec: 1-F, 1.26; 1-Cl, 1.56; 1-Br, 1.80; 1-NO_2, 2.28; 1-$COCH_3$, 2.49).

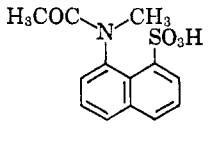
D. OPTICAL RESOLUTION

In view of the short distance between the *peri* positions in naphthalene, one might expect restriction of rotation in compounds with sizable *peri* substituents; when conditions are favorable, such compounds should manifest optical activity and give rise to optical isomers. Some of the early examples wherein this expectation has been fulfilled are discussed by Jamison (301). One such case is the resolution (424) of 8-nitro-1-naphthyl-N-benzenesulfonylglycine (XLVII). The fact that the optical activity of XLVIIa is critically associated with *peri* hindrance due to the nitro group is realized by the loss of activity when the *peri*-nitro group is replaced by hydrogen (XLVIIb). Subsequently, a number of similar cases have appeared in the literature (Table XIII).

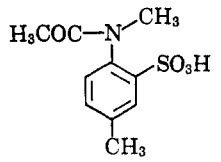


XLVII a, R = NO_2
b, R = H

Mills and Elliott (424) have pointed out that the optical stability of *peri*-naphthalene derivatives is much less than that of di(*ortho*-substituted)biphenyls and deduce that hindrance to rotation in biphenyls is more pronounced than in *peri*-substituted naphthalenes. Mutually contrary findings (4, 425) on this point suggest that the answer depends on the detailed geometry of the system. Mills and Kelham (425) have estimated the critical energy increment for racemization in XLVIII (26.9 kcal/mole) and in the analogous benzene derivative XLIX (22.6 kcal/mole). On this basis they conclude that the restrictive effect of *peri* interaction between contiguous substituents should be greater than

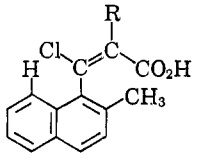


XLVIII

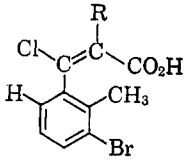


XLIX

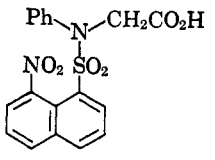
that from *ortho* overlap. Adams and Binder (4) on the other hand have considered the optical stability of the sterically more closely related structures L and LI. LIa does not racemize and LIb has a half-life of 200 min.



La, R = CH_3
b, R = H



LIa, R = CH_3
b, R = H

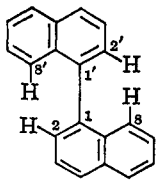


LII

The naphthalene derivative La does racemize ($t_{1/2}$ = 70 hr in boiling butanol) and Lb has an even shorter half-life (70 min). This led them to suggest that the steric effect of an *o*-methyl group is larger than that of a *peri*-methine group.

Following Mills and Elliott's observation about the optical activity of XLVIIa, it was predicted (525) from a study of molecular models that LII should also be resolvable. In spite of the possible overlap of the van der Waals envelopes of the adjoining groups, attempts to resolve LII did not succeed. Rule and Turner (503) have successfully resolved 8-carboxy-1-naphthyl phenyl sulfoxide, but this resolution is undoubtedly dependent on the presence of the dissymmetric sulfoxide function.

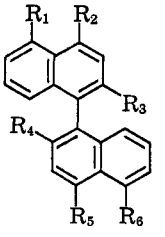
A vast amount of work has been published on the optical resolution and stability of 1,1′-binaphthyl and its derivatives. Even though binaphthyl itself eluded optical resolution till 1961, there had appeared several studies devoted to its derivatives. The origin of optical activity in this series of compounds is in the restriction to free rotation of the naphthyl units about the coannular bond as a result of interference between 2 and 8′ and 2′ and 8 substituents (LIII).



LIII

Bell and Waring (67) resolved 1,1′-bianthryl and predicted (69) that 1,1′-binaphthyl should also be resolvable. In these compounds, the β-hydrogen and the *peri*- or *meso*-hydrogen just overlap when their covalent radii are considered, but they interfere strongly if their van der Waals radii are taken into account. The authors did indicate (69) that the optical stability of binaphthyl would be much less than that of bianthryl. However, they did not succeed in resolving the former compound (67). Crawford and Smith (147, 148) have examined the optical activity of biquinolyls (147) and biisoquinolyls (148). They have partially resolved 4,4′- and 5,5′-biquinolyls through their tartrate salts, but the ease of racemization of these compounds was too great to isolate the pure enantiomers. The optical instability of 1,1′-, 4,4′-, and 5,5′-biisoquinolyls is even greater. These experiments nevertheless indicated the possible resolution of 1,1′-binaphthyl. In accordance with this expectation, Harris and Mellor in 1961 obtained (258) (+)-1,1′-binaphthyl with a half-life of 13 min at 50° in dimethylformamide solution. The half-life reported (66, 67) for 1,1′-bianthryl is 60 min in boiling chloroform (61°). It is worthwhile to mention that two crystalline modifications of 1,1′-binaphthyl have been isolated recently (42).

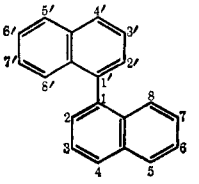
A large number of binaphthyl derivatives have been resolved by several workers. Stanley (523) has observed that, when once resolved, 2,2′-dicarboxy-1,1′-binaphthyl (LIVa) is quite resistant to racemization. Thus its optical rotation does not change on heating at 175° in dimethylformamide for 8 hr, for 2 hr in boiling tetralin (250), or by heating in alkaline solution (248, 357). The 5,5′-dicarboxylic acid (LIVb) has also been resolved (70, 71) through its brucine salt, and its optical stability is considered comparable to that of 1,1-bianthryl but much less than that of the 2,2′-dicarboxylic acid (LIVa) or the 2,2′-diamine (LIVe). Hall, Ridgwell, and Turner (249) have also resolved LIVb and found that it undergoes complete racemization on boiling for 1 hr in 0.1 *N* sodium hydroxide solution. The



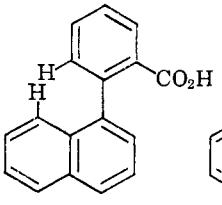
LIVa, $R_1 = R_2 = R_5 = R_6 = H$; $R_3 = R_4 = CO_2H$
b, $R_2 = R_3 = R_4 = R_5 = H$; $R_1 = R_6 = CO_2H$
c, $R_1 = R_3 = R_4 = R_6 = H$; $R_2 = R_5 = NH_2$
d, $R_1 = R_3 = R_4 = R_6 = H$; $R_2 = R_5 = CO_2H$
e, $R_1 = R_2 = R_5 = R_6 = H$; $R_3 = R_4 = NH_2$

relatively high optical stability of this compound occasions surprise because hindrance to free rotation in this compound is probably not different from that in binaphthyl itself. 1-(*o*-Carboxyphenyl)naphthalene (LV) has also been resolved, but its optical stability is very low ($t_{1/2}$ = 2 min at 20° in chloroform) (249). Also it has not been possible to resolve either 1-phenylnaphthalene or its derivatives such as LVI or LVII (249). Apparently, a simultaneous *o,o*′-biphenyl-type interaction (*e.g.*, COOH–H) is needed.

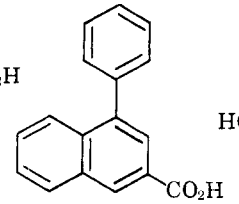
TABLE XIV
RACEMIZATION DATA OF SOME 1,1′-BINAPHTHYLS



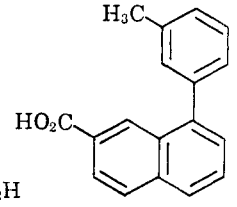
Substituents	$t_{1/2}$, min	Temp, °C	Solvent	E_{rac} (kcal/mole)	Ref
None	14.5	50	DMF	22.5	538
	13.0	50	DMF	22.5	258
4,4′-$(NH_2)_2$	180–240	Room temp	60% acetone	21.4	538
4,4′-$(NH_2)_2$	5.8	50	DMF	21.9	41
5,5′-$(CO_2H)_2$	271.5	50	DMF	24.1	141
5,5′-$(CO_2^-)_2$	33	60	0.1 *N* NaOH	...	249
5,5′-$(CO_2^-)_2$	94	50	0.1 *N* NaOH	24.9	141
5,5′-$(CO_2Me)_2$	101	50	DMF	23.8	141
8,8′-$(CO_2H)_2$	51.5	50	DMF	22.1	41
	160	20	Aq NaOH	...	419
8,8′-H, CO_2H	15.4	50	DMF	22.4	41
	900.0	20	Aq NaOH	...	419
8,8′-$(CO_2^-)_2$	3.0	50	0.1 *N* NaOH	26.0	141
8,8′-$(CO_2Me)_2$	23.0	50	DMF	22.0	41
8,8′-CO_2H, -CO_2Et	18.3	50	DMF	21.6	41
	1680	18	Aq NaOH	...	419
8,8′-CO_2^-, -CO_2Et	31.0	50	0.1 *N* NaOH	23.7	141
8,8′-CO_2Me, CH_2OH	14.1	100	DMF	25.8	41
8,8′-$(CH_2OH)_2$	395	100	DMF	29.2	41
8,8′-$(CH_3)_2$	679	100	DMF	27.6	40



LV



LVI



LVII

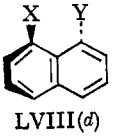
Only negative results were reported in attempted resolutions of 4,4′-diamino- (LIVc) and 4,4′-dicarboxy- (LIVd) 1,1′-binaphthyl (69). However, the diamine LIVc has since been resolved (41, 538). Data on the optical stability of a number of binaphthyls that have been investigated are collected in Table XIV.

The remarkable ease of racemization of 8,8′-dicarboxy-1,1′-binaphthyl as contrasted to the 2,2′-dicarboxylic acid LIVa, in spite of comparable restrictions to rotation in both of them, has been pointed out in several papers (41, 71, 141, 257, 259, 523). Bell and Morgan (71) suggested that racemization of the 8,8′-dicarboxylic acid probably occurs through preliminary dissociation into naphthyl radicals rather than through a planar transition state since the latter process should demand a high activation energy. This view is said to be supported by the increase in racemization rate with temperature.

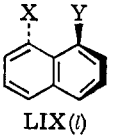
Another view (141, 257, 259) is that the optical instability of the 8,8′-diacid is caused by intramolecular crowding which induces a state of strain in the molecule that is relieved by molecular distortions. The effect of these distortions is favorable to optical inversion by reducing the rotational energy barrier through increase of ground-state energy (257). The energy barrier for racemization (E_{rac}) has been discussed in terms of E_{steric}, E_r, and E_{gs} where E_{steric} represents the energy due to strain and compression in the transition state, E_r the gain in resonance energy in the transition state, and E_{gs} the ground-state energy. Their relationship may be written as

$$E_{rac} = E_{steric} - E_r - E_{gs}$$

The possibility of ground-state strain being a significant factor in the observed optical lability of 8,8′-dicarboxy-1,1′-binaphthyl is also suggested. The arguments of the Harris school concerning the strained conformation of 8,8′-disubstituted 1,1′-binaphthyls may be stated in the following terms: any *peri*-substituted naphthalene, 1,8-$C_{10}H_6XY$, with C_8–X and C_1–Y bonds forced out of plane with one of them above and the other below the mean plane of the nucleus, may be theoretically represented in two diastereoisomeric structures LVIII and LIX. When these units combine to make 1,1′-binaphthyl, there can be three readily interconvertible



LVIII(*d*)



LIX(*l*)

forms *dd*, *ll*, and *dl*, each of which in turn can lead to *R* and *S* configurational isomers by rotation about the 1,1′ bond. The inversion of such structures of 8,8′-disubstituted derivatives through the "*trans* route" involves much less strain than for 2,2′-dicarboxylic acid, for example. The steric compression energy for 1,8-dimethylnaphthalene is estimated as 7.9 kcal/mole (468). Assuming two such interactions in the 8,8′-dicarboxylic acid, a value of ~15 kcal/mole is suggested as a lower limit for the ground-state strain energy in this molecule. An even more elaborate mechanistic approach has been made to study the optical instability of this compound (41, 141, 257, 259).

Optical activity is observed in several other overcrowded derivatives of phenanthrene and anthracene which may be formally regarded as *peri*-naphthalene derivatives. As has been pointed out by Newman (438, 447), optical activity may be expected in molecules where dissymmetry is caused either by out-of-plane bending of parts of the molecule or by a distortion of the nucleus. This is an important distinction between optically active biphenyls and overcrowded aromatic compounds. In the former, the phenyl rings themselves remain flat and coaxial even though they are not coplanar. A partial list of the latter, *i.e.*, overcrowded optically active systems, includes 4,5,8-trimethylphenanthrene-1-acetic acid (442, 443), 1-methylbenzo[*c*]phenanthrene-4-acetic acid (444), 1,12-dimethylbenzo[*c*]phenanthrene-5-acetic acid and its methyl ester (447), 3,4,5,6-dibenzophenanthrene-9,10-dicarboxylic acid (66, 68), 3,4,5,6-dibenzo-9,10-dihydrophenanthrene (248), 4′,4″,6′,6″-tetramethyl-3,4,5,6-dibenzo[*c*]phenanthrene-9,10-dicarboxylic acid (68), 1,1′-bianthryl (67), 2,2′-diamino-1,1′-bianthryl (67), 9,9′-bianthryl-3,3′-dicarboxylic acid (68), 10-(*o*-carboxyphenyl)-1,2-benzanthracene (558), and hexahelicene (448).

From a study of the rates of racemization of 9,10-dihydro-4,5-dimethylphenanthrene and its deuterated isomers, deuterium is shown to have a smaller steric requirement than hydrogen (427).

E. COMPLEX FORMATION

Comprehensive reviews (12, 439, 463) and at least one monograph (13) are available on molecular complexes of organic compounds. The stability of the complex depends upon the steric and electronic properties of the acceptor and donor molecules. The formation of the complex is greatly facilitated when (i) the donor molecule has electron-releasing substituents, (ii) the acceptor molecule has electron-attracting substituents, and (iii) both donor and acceptor molecules are planar. For example, polynuclear aromatics with their readily polarizable π-electron systems are an important class of donors, and polynitro aromatic compounds such as picric acid, trinitrobenzene (TNB), 2,4,7-trinitrofluorenone (TNF), and 2,4,5,7-tetranitrofluorenone function as useful acceptors. More recently, benzotrifuroxan has also been introduced for this purpose (50, 52, 53).

The normal substituent effects in the acceptor and donor molecules tend to become modified when substituents introduce steric strain in the molecule (12, 13, 439, 463). Thus α- and *peri*-substituted naphthalenes, and analogous derivatives in which the planarity of the molecule is often disrupted, form adducts only with the more powerful complexing agents, the weaker ones giving either an unstable derivative or none at all. The stability of these complexes is judged either from their melting points[3] or association constants defined by

$$K = \frac{[\text{complex}]}{[\text{acceptor}][\text{donor}]}$$

and the related free energies of formation ($\Delta G = -RT \ln K$). Data obtained with regard to complex formation of a number of naphthalene derivatives are reviewed in this section with particular reference to the effect of *peri* substituents.

Bailey, Pickering, and Smith (51) prepared TNB complexes from a series of 1- and 2-alkylnaphthalenes, the straight-chain alkyl group varying from methyl to *n*-hexyl. There does not seem to be any significant difference in the stability of the 1 and 2 series as judged from their melting points. This would seem to suggest that the *peri*-hydrogen interaction with straight-chain 1-alkyl groups is not serious.

A later and more extensive study of the association constants of a number of 1- and 2-monosubstituted naphthalenes for picrate formation has been made by partition (232) and spectrophotometric (233) methods. A summary of these results is given in Table XV. The stability of the complex decreases as the alkyl group varies from methyl to ethyl to isopropyl. Furthermore, the association constant suffers a larger decrease in the 1-alkyl series than in the 2- series. This is presumably due to the steric effect of 1-alkyl group being augmented by that of *peri*-hydrogen which is absent in the 2-alkyl series. It must, however, be noted that there is evidence of stable picrates being isolated from not only 2-*t*-butylnaphthalene but also the 1 isomer (233, 293, 332, 336). On steric considerations alone, the formation of a stable complex from the latter would seem to be difficult.

(3) Shinomiya (515) made a series of investigations on complex formation of several types of organic substrates with picric acid. On the basis of this and other studies, Orchin (463) suggested that the melting point of the complex may be used as a criterion of its stability probably because of the possibility of larger polar character of the complex with increasing donor–acceptor interaction leading to an increased melting point. The equilibrium involved in the melting process will be affected by both the charge-transfer interaction and by crystal lattice forces. Estimation of complex stability through spectrophotometric methods in solution are perhaps more precise. From an inspection of a large body of data, it appears difficult to draw conclusions as to whether or not the melting points are a reliable index to estimate the steric strain in the donor substrate (326, 332, 537).

TABLE XV
ASSOCIATION CONSTANTS OF PICRATES IN CHLOROFORM (28.5°)

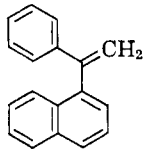
	Association constant (l. mole^{-1})			
	Partition method (232)		Spectrophotometric method (233)	
Substituent	1-Position	2-Position	1-Position	2-Position
H	2.31	2.31	1.13	1.13
Me	3.16	3.50	1.47	1.76
Et	2.61	2.77	1.41	1.45
Pr-*i*	1.87	2.51	0.97	1.35
Bu-*t*	...	...	...	1.16
F	1.49	1.28	0.55	0.33
Cl	1.87	1.50	0.43	0.34
Br	2.06	1.57	0.51	0.43
I	2.13	1.62	...	...
OMe	4.89	3.30	2.78	1.48
OEt	5.78	3.01	3.76	2.11
OPr-*i*	4.81	3.09	2.87	1.66
COMe	2.76	2.47	...	...
CH=CH$_2$	...	...	2.13	1.79

An interpretation of the above data obtained with the halo- and alkoxy derivatives does not seem so simple. The absence of a pronounced steric effect with increasing size of the 1-substituent may be explained by invoking the increasing polarizabilities of the halogens (F > Cl > Br > I) which presumably override *peri*-hydrogen hindrance to complex formation. The case with the acetyl compounds is interesting. There is a clear indication (55, 366, 493) that the acetyl group at the 1-position is twisted out of plane. As such, it should be expected to exert only an inductive effect which should lead to a decrease of complex strength. On the contrary, the complex from 1-acetylnaphthalene is as strong as that from 1-ethylnaphthalene. The reason for this appears to be that the carbonyl group functions as a localized donor (232).

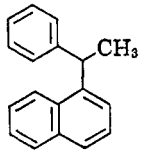
A series of investigations have been made (326, 328) on the complexing behavior of 1- and 2-substituted naphthalenes with TNF. Data for the apparent stability constants of these derivatives as well as the angles of twist estimated for the substituents from the molecular plane are presented in Table XVI.

The apparent stability constants for 1-cyclohexenylnaphthalene complexes are considerably lower than those of the 2 isomers. This is attributed to two factors: (i) a better donor–acceptor overlap in the 2 series than in the 1 series by virtue of the substituent positions and (ii) reduced coplanarity of the 1-cycloalkenyl group with the nucleus due to *peri*-hydrogen interaction. A comparison of the values observed for the series 1-methyl- (27.5), 1′-cyclopentenyl-(21.6), 1′-cyclohexenyl-(16.0), 2′-methyl-1′-cyclopentenyl- (15.2), and 2′-methyl-1′-cyclohexenyl- (9.5) 1-naphthalenes clearly indicates the profound influence of steric factors on complex stability. This is also reflected in the increased angles of twist of the 1-substituents with increasing bulk.

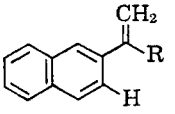
The complex stabilities of a few related vinylnaphthalenes have also been studied (101, 328, 335). Taking the melting point range and effect of solvents as criteria for stability, it is found that 1-(1′-naphthyl)-1-phenylethylene (LX) and its saturated derivative (LXI) either did not form a picrate or gave one that was unstable, readily decomposing even on attempted crystallization. The corresponding derivatives from



LX



LXI



LXII

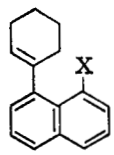
the 2 isomers were well defined and stable. Here again, the *peri*-hydrogen effect is responsible in weakening the complexes derived from LX and LXI (101). In 2-vinylnaphthalenes (LXII), the stability seems to be affected by the increasing bulkiness of R; the complex formation is totally suppressed with R = *t*-Bu. The deterrent in this case is the C$_3$ hydrogen (335).

Mention may be made of yet another study on 1-cycloalkenylnaphthalenes (329). While the bromo compound LXIIIa fails to yield a crystalline picrate or

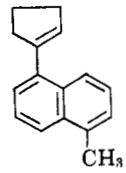
TABLE XVI
APPARENT STABILITY CONSTANTS (K_s)[a] FOR 1:1 COMPLEXES OF 1- AND 2-SUBSTITUTED NAPHTHALENES WITH TNF IN ACETIC ACID AT ROOM TEMPERATURE (326, 328)

	K_s		Angle of twist, deg	
Substituent	1-Position	2-Position	1-Position	2-Position
H	17.0	17.0	0	0
Me	27.5	27.6	0	0
Br	21.5	16.0	0	0
COMe	17.9	14.7	42 or 65	0
CH=CH$_2$	28.7	31.5	36 or 65	0
Cyclopentenyl	21.6	64.0	44	0
Methylcyclopentenyl	15.2	29.7	50–75	0
Cyclohexenyl	16.0	50.5	52 or 80	0
Methylcyclohexenyl	9.5	16.3	78 (axial methyl) 85 (equatorial methyl)	0

[a] The authors define the apparent stability constant as $K_s = C_c/[N_H(C_{to} - C_c)]$, where C_c = molar concentration of the complex, C_{to} = total concentration of TNF, and N_H = mole fraction of free hydrocarbon at equilibrium.



LXIIIa, X = Br
b, X = CH_3



LXIV

TNB derivative, the methyl compound LXIIIb does yield a TNB derivative though with a wide melting range (105–135°). The melting range is not much better for LXIIIb picrate (96–111°) or the TNB derivative (103–111°) of LXIV (329). The case turns out to be different either when the substituent is a saturated five- or six-membered ring or a larger ring (seven- or eight-membered) even if unsaturated. It is thus found that 1-cyclohexylnaphthalene forms a fairly stable picrate (140, 517) as do 1-naphthylcycloheptene and 1-naphthylcyclooctene (331). This seems to suggest a puckering of the cycloalkenyl rings in the latter examples so as to avoid *peri* interactions. These observations may be contrasted with the nonformation of complexes with 1-phenylnaphthalene (50, 140, 221, 517).

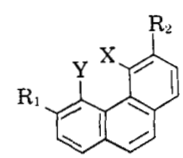
A number of reports (1, 60, 336, 382, 429) have appeared from various workers on the isolation of molecular complexes of polymethylnaphthalenes. A perusal of the available compilation (171) of the melting points of these complexes, especially of *peri*-methylnaphthalenes, provides an interesting study. They are in general 1:1 complexes. Considering the suggested nonplanarity of *peri*-dimethylnaphthalene system (170, 213, 300), the apparent stability of these complexes is remarkable. In the extreme case of octamethylnaphthalene, a severe deviation of the molecule from planarity has been clearly established from crystal structure studies (170). Abadir, Cook, and Gibson (1) have, however, characterized the picrate, styphnate, and TNB complexes of octamethylnaphthalene, and there is no evident note of any difficulty in their formation or isolation. Perhaps, despite the severe molecular distortion, the inductive effects of the methyl groups override the effects due to loss of planarity, thus promoting complex formation.

In the case of phenylnaphthalenes, the less-hindered 2-phenylnaphthalene forms a 2:1 complex with TNB that is easily dissociated and hence difficult to purify (221). In 2-(*o*-tolyl)naphthalene a biphenyl-type of steric hindrance comes into play, preventing complex formation with picric acid or TNF; however, a 2:1 complex with trinitrobenzene has been isolated (221). Attempts to prepare similar TNB or TNF complexes with the 1-phenyl isomer did not succeed (50, 465); nevertheless, the more powerful acceptor benzotrifuroxan does form a stable 1:1 complex with 1-phenylnaphthalene (50, 52).

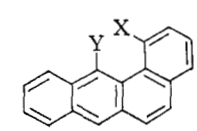
1,5-Diphenylnaphthalene, containing two α-phenyl substituents, fails to form a similar complex with any of these reagents. For example, on mixing hot solutions of the 1,5-diphenyl compound and benzotrifuroxan, a yellow color develops, but cooling the mixture causes the separation of the hydrocarbon. The nonformation of a crystalline adduct is attributed to the noncoplanar structure of the donor molecule (50, 53). A similar explanation appears valid in the case of 1,7-diphenyl- and 1-phenyl-7-*o*-tolylnaphthalenes. The behavior of 1,8-diphenylnaphthalene should then be considered exceptional since it is known to form a crystalline, though unstable, complex with benzotrifuroxan (53). There is increasing evidence to show that in molecules like 1,8-diphenylnaphthalene, the *peri*-phenyl rings are almost perpendicular to the naphthalene plane and parallel to each other (53, 225, 281, 299). Further results from work directed to the preparation of sandwich compounds of 1,8-diphenylnaphthalene by House (280) should indeed be of much interest. The situation with respect to other di- and polyphenylnaphthalenes cannot be usefully reviewed since no pertinent data are available in literature.

The results on the equilibrium constants and the free energy of formation of the dinitronaphthalene–*p*-bis(dimethylamino)benzene complex (186) provide a better correlation between the expected and observed results. Among the dinitronaphthalenes, steric hindrance may be expected to increase with the increasing proximity of the nitro substituents, being maximum in the *peri*-dinitro compound. The stability may therefore be expected to fall in the order *peri* < *ortho* < other positions. That this indeed is the case may be examined from the figures in Table XVII. The value of $-\Delta G$ drops from the least hindered 2,7 and 2,6 isomers (860 and 690 cal/mole, respectively) to the most hindered 1,8-dinitro compound (50 cal/mole). One may be tempted to attribute this effect entirely to steric reasons. At least part of the weakening in these complexes is caused by the greater electronegativity of the β-nitro group over that of the α-nitro group, however, as is evident in a comparison of the 1,5 with the 2,6 isomer, for example.

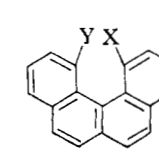
Several reports (130, 445, 446, 450, 463, 465, 537) are available in the literature concerning the complex formation of other related systems like 4,5-substituted phenanthrenes (LXV), 1,2-benzanthracenes (LXVI), and benzo[*c*]phenanthrenes (LXVII). The available data do not seem to permit any generalization of the complexing behavior in terms of steric or electronic fac-



LXV



LXVI



LXVII

TABLE XVII
EQUILIBRIUM CONSTANTS (K) AND FREE ENERGIES OF FORMATION ($-\Delta G$) FOR COMPLEX FORMATION BETWEEN DINITRONAPHTHALENES AND *p*-BIS(DIMETHYLAMINO)BENZENE IN CYCLOHEXANE AT 22° (186)

Dinitronaphthalene	K, l./mole	$-\Delta G$, cal/mole
2,7-	4.32	860
2,6-	3.24	690
1,3-	3.12	660
1,7-	2.50	540
1,6-	2.24	460
2,3-	2.01	400
1,4-	1.81	350
1,2-	1.28	160
1,5-	1.12	60
1,8-	1.08	50

tors. Even such compounds as 3,4,5,6-tetramethylphenanthrene (LXV, $R_1 = R_2 = X = Y = CH_3$) where buttressing effects may worsen the already overcrowded situation in the molecule are found to form sharp-melting TNB derivatives (440).

F. DISSOCIATION CONSTANTS

The effect of steric influences on the dissociation constants of organic acids and bases has been extensively studied and reviewed (103, 164, 253, 583, 585). As is the case with other properties, the dissociation constants of 1- and 2-naphthoic acids, naphthols, and naphthylamines show considerable distinctions between the two series. This is true of the positional isomers of other related polycyclic derivatives as well.

Lauer (363) has determined the "electrolytic dissociation constants" of a number of polynuclear aromatic carboxylic acids (Table XVIII). The hindered acids display higher values when compared to the nonhindered ones.

TABLE XVIII
ELECTROLYTIC DISSOCIATION CONSTANTS (H_2O, 20°) (363)

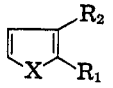
Compound	$K \times 10^5$
Benzoic acid	6.00
1-Naphthoic acid	20.30
2-Naphthoic acid	6.80
9-Anthroic acid	22.60
1-Anthroic acid	20.62
2-Anthroic acid	6.68

TABLE XIX
THERMODYNAMIC DISSOCIATION CONSTANTS (H_2O, 25°) (165, 166)

Compound	$K_{th} \times 10^5$
Benzoic acid	6.27
o-Ethylbenzoic acid	16.1
o-Isopropylbenzoic acid	23.1
o-(*t*-Butyl)benzoic acid	29.2
2,6-Dimethylbenzoic acid	56.8
1-Naphthoic acid	20.2
2-Naphthoic acid	6.90
Phenylacetic acid	4.88
1-Naphthylacetic acid	5.81
2-Naphthylacetic acid	5.55

Later, Dippy, Hughes, and Laxton (165) determined the dissociation constants of 1- and 2-naphthoic acids as well as a number of *o*-alkylbenzoic acids for comparison. Their data are given in Table XIX. The higher acid strength of 1-naphthoic acid is attributed to the steric effect of *peri*-hydrogen which presumably twists the 1-carboxyl group out of the ring plane, thereby inhibiting the resonance stabilization of the free acid and thus making it less stable *vis-à-vis* the anion ("steric inhibition of resonance"). This has been pointed out by other workers also (82, 213, 279).[4] As judged from the figures of Table XIX, the steric effect of *peri*-hydrogen appears to be intermediate between the effects for *o*-ethyl and *o*-isopropyl groups. When the carboxyl group is insulated from the naphthalene ring by interposing a methylene group as in 1- and 2-naphthylacetic acids, the dissociation constants are seen to be quite close since there is no longer resonance of the 1- or 2-carboxyl with the ring and hence no possibility of steric inhibition. The view that steric effects persist in spite of an intervening methylene group is advanced from a study of the hydrolysis of esters derived from the isomeric naphthoic and naphthylacetic acids (2). The two views are not contradictory, since in esterification and hydrolysis (unlike in anion formation) a tetrahedral intermediate is involved and primary steric hindrance effects (*i.e.*, crowding in the transition state) may occur in both $ArCOOH$ and $ArCH_2COOH$.

A linear correlation is reported (467) between the rates of hydrolyses of the esters derived from 3-furoic acid (LXVIIIa), 3-thenoic acid (LXVIIIb), and 2-naphthoic acid and the dissociation constants of the free acids. No such correlation seemed to hold for the



LXVIII a, X = O; R_1 = H; R_2 = CO_2H
b, X = S; R_1 = H; R_2 = CO_2H
c, X = O; R_1 = CO_2H; R_2 = H
d, X = S; R_1 = CO_2H; R_2 = H

corresponding data on 2-furoic (LXVIIIc), 2-thenoic (LXVIIId), and 1-naphthoic acids, presumably due to aforesaid reasons (hydrolysis is affected by steric factors in the latter compounds).

Price, Mertz, and Wilson (483) have studied the dissociation constants of a few derivatives of 1-naphthoic and 2-thenoic acids. The strong acid-strengthening effect of the *p*-nitro group observed in *p*-nitrobenzoic acid is considerably diminished in 4-nitro-1-naphthoic and 5-nitro-2-thenoic acids. That this difference is due to steric inhibition of resonance of the nitro group is indicated by the absence of any such deviation in the corresponding methyl and chloro acids.

(4) For a less probable explanation involving a dipole-induced dipple interaction of COO^- and aromatic H, see Lauer (363).

In this context, the results of Hoop and Tedder (279) are of interest. These authors have discussed the dissociation constants of 1- and 3-halo-2-naphthoic acids (Table XX). In these compounds, while the inductive

TABLE XX
DISSOCIATION CONSTANTS ($K \times 10^6$) OF HALOBENZOIC AND NAPHTHOIC ACIDS (71% ETHANOL, 25°) (279)

Substituent (X)	o-$XC_6H_4CO_2H$	1,2-$XC_{10}H_6CO_2H$	3,2-$XC_{10}H_6CO_2H$
H	0.58	0.79	0.79
F	3.30	7.60	4.30
Cl	7.30	12.00	8.20
Br	9.20	16.00	9.50

effect of the halogen may be considered to be approximately the same, there would be a significant difference in their mesomeric interaction. The latter is greater for a 1-halogen than for a 3-halogen as a result of bond fixation in naphthalene. Consequently, 1-halo-2-naphthoic acids would be expected to be weaker than the 3-halo isomers. It, however, turns out that the 1-halo acids are nearly twice as strong as the benzene analogs, whereas the 3-halo acids are only very slightly stronger than the corresponding *o*-halobenzoic acids. The abnormal increase in acid strength in the case of 1-halo acids is attributed to a loss of mesomeric interaction of 1-halogens due to a permanent bending out of the molecular plane. Inductive effect variations alone are not considered sufficient to cause such a large difference in the acid strengths. The postulated out-of-plane bending of the sterically hindered halogen in the naphthalene derivative would be justifiable in view of the known distortion of the chlorine atom in *o*-chlorobenzoic acid (195). In-plane movement of 1-halogen is not likely since such a movement would interfere with the planarity of the carboxyl group with the ring.

The pK_a values of a number of alkylnaphthoic and acenaphthoic acids (Table XXI) have been measured in 70% dioxane (213). The introduction of an *o*-

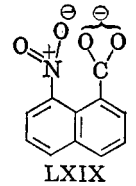
TABLE XXI
pK_a's OF METHYLNAPHTHOIC ACIDS AND ACENAPHTHOIC ACIDS (70% DIOXANE, 25°) (213)

Compound	pK_a
1-Naphthoic acid	4.53
2-Naphthoic acid	4.89
4-Methyl-1-naphthoic acid	4.81
5-Methyl-1-naphthoic acid	4.57
1-Methyl-2-naphthoic acid	4.42
4-Methyl-2-naphthoic acid	4.98
4,5-Dimethyl-1-naphthoic acid	4.61
1,8-Dimethyl-2-naphthoic acid	4.25
4,5-Dimethyl-2-naphthoic acid	5.00
3-Acenaphthoic acid	5.49
4-Acenaphthoic acid	5.08
5-Acenaphthoic acid	5.30

methyl group in position 1 lowers the pK_a of 2-naphthoic acid by 0.47 unit as compared to 0.30 unit in *o*-toluic acid. The larger decrease in the naphthalene case is attributed to the buttressing effect of the *peri*-hydrogen. This view is supported by the even larger ΔpK_a (−0.64) observed for 1,8-dimethyl-2-naphthoic acid. The buttressing of the 8-methyl substituent would cause an in-plane deviation of the 1-methyl toward the carboxyl group, with resulting enhancement of steric inhibition of resonance.

The data on 4,5-dimethyl-1-naphthoic acid are also interesting. The additivity of the effects due to 4-methyl and 5-methyl substituents is said to hold well for 4,5-dimethyl-2-naphthoic acid but breaks down in 4,5-dimethyl-1-naphthoic acid. In the latter case, the observed ΔpK_a is only 0.08 instead of the expected 0.32. Such a breakdown of additivity relationships under severe steric compression has also been pointed out in the benzene series (83, 530).

Berliner and Winicov (82) have potentiometrically determined the apparent dissociation constants of 13 out of the 14 possible nitronaphthoic acids at 25° in 50% Cellosolve solution. Of all the isomeric nitronaphthoic acids, only the 2,6 and 2,7 acids will be totally devoid of *ortho* and/or *peri* interactions. These effects are attenuated in 1-nitro-2-naphthoic, 2-nitro-1-naphthoic, and 8-nitro-1-naphthoic acids. Compared to the unsubstituted acids, both 2-nitro-1- (pK_a = 3.96) and 1-nitro-2- (pK_a = 4.53) naphthoic acids are stronger. The lower acidity of the latter is attributed to a reduction in the acid-strengthening effect of the nitro group. It would then appear that hindrance to planarity affects both a 1-nitro group and a 1-carboxyl. Steric inhibition of resonance when acting on COOH is acid strengthening but when acting on NO_2 is acid weakening. In 3,1, 4,2, and 8,1 acids, the relative disposition of the groups may be considered *meta*. In these cases only the inductive effect of the nitro group is operative. The smaller ΔpK_a (0.64) in the case of the *peri*-nitro acid compared to those in 3,1 (0.89) and 4,2 (0.98) acids is suggested to be a steric inhibition of resonance effect (82). It is perhaps worthwhile to consider a possible alternative, namely, that repulsive forces in the anion of the 1,8 acid destabilize it.



LXIX

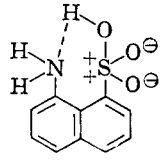
Wells and Adcock (579a) have just published their findings on the dissociation constants of a large number of substituted 1- and 2-naphthoic acids. Except in the case of 2,6 and 2,7 acids, the observed values seem to be affected by *peri* effects. Another recent report (213a) discusses the dissociation constant of 8-chloro-1-naphthoic acid. In 20% dioxane solution, the pK_a for the 8-chloro acid is 4.43 while the value for 1-naphthoic acid is 4.53. This is attributed to steric hindrance to solvation.

TABLE XXII
pK_a VALUES OF SOME SUBSTITUTED PHENOLS AND CARBOXYLIC ACIDS (H_2O, 25°) (149)

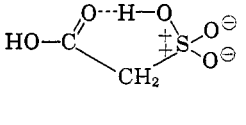
Substituent (1)	Phenol (2)	1-Naphthol (3)	ΔpK (2) − (3)	Benzoic acid (4)	Naphthoic acid (5)	ΔpK (4) − (5)
H	9.99	9.39	0.60	4.20	3.64	0.56
3-CH_3	...	...	...	4.27	3.72	0.55
4-CH_3	10.26	9.64	0.62	...	...	...
3-NO_2	8.40	7.86	0.54	3.49	2.83	0.66
4-NO_2	7.15	5.73	1.42	3.42	2.80	0.62
4-F	...	...	...	4.14	3.70	0.44
4-Cl	9.42	8.86	0.56	4.97	3.36	1.61
4-Br	9.36	8.72	0.64	4.97	3.37	1.60
4-OCH_3	...	...	...	4.47	4.31	0.16
4-CN	7.97	7.08	0.89	...	...	...
4-CHO	7.41	6.53	0.88	...	...	...
4-COC_6H_5	7.95	7.33	0.62	...	...	...

The pK_a's of a number of 4-substituted 1-naphthoic acids and 1-naphthols in aqueous solution have also been measured and compared with those of the corresponding benzoic acids and phenols (149) (Table XXII). The difference in pK values between structurally related pairs of compounds may be expected to be nearly equal in the absence of other complicating steric or electronic effects. The data in Table XXII are in general accord with this expectation. However, the deviation observed for 4-chloro- and 4-bromo-1-naphthoic acids is notoriously large and has not been explained. The agreement observed for 4-benzoyl-1-naphthol is fortuitous. It appears that the effect of steric hindrance to mesomerism of the benzoyl group just balances the extra resonance effect resulting from the presence of an additional fused ring, but in 4-nitro-1-naphthol the steric effect is inadequate to mask the extra resonance (149). The need to consider *peri* effects in discussing the dissociation constants of substituted 1- and 2-naphthols has been emphasized by some other workers too (87, 113).

Bryson (109, 110) has made a study of the strengths of the conjugate acids derived from several nitronaphthylamines (109) and naphthylaminesulfonic acids (110). In the latter series, the 1,8 acid with a pK_a of 5.03 is the weakest of the series; the pK_a's for all the other members are in the range 1.71–3.92 for the 1-amines and 2.35–4.11 for the 2-amines. The possibility of a hydrogen-bonded structure (LXX) is suggested for the *peri* isomer on the analogy with a



LXX



LXXI

similar structure (LXXI) in $HO_2C{\cdot}CH_2{\cdot}SO_3H$ (96).

Among the nitronaphthylamines, the pK_a of 8-nitro-1-naphthylamine is found to be 2.79 while those of the related derivatives (*i.e.*, those heteronuclear derivatives where the substituents are in nonquinonoidal positions) are in the neighborhood of 3.15. This is explained to result from a widening of the angle between the dipoles due to C–NO_2 and C–NH_2 (109), but a field effect might provide an alternative cause.

Of the polycyclic aromatics related to *peri*-substituted naphthalenes, benzo[*c*]phenanthrylamines have been investigated by Newman and Blum (452). The ionization constant (in 50% ethanol) of the 1-amine (LXVII, X = NH_2, Y = H) (2.78) is much lower than those of the other isomers (3.10–3.66). This is attributed to steric hindrance to solvation of the protonated amine. The observed data also indicate that the 2- and 3-amines are not hindered while the 4-, 5-, and 6-amines are comparable to 1- and 9-phenanthrylamines which are also subject to steric effects of the fused ring. The pK_a values of isomeric phenanthrols and benzo[*c*]-phenanthrols have likewise revealed (451) that 4-phenanthrol (LXV, X = OH, Y = H) and 1-benzo[*c*]-phenanthrol (LXVII, X = OH Y = H) are the weakest in each series; obviously, anion solvation may be expected to be less facile in these cases.

Steric inhibition of resonance is seen in studies of phenanthroic acids (449). 4-Phenanthroic acid (LXV, X = CO_2H, Y = H; pK_a = 5.43) is stronger than even *o*-(*t*-butyl)benzoic acid (pK_a = 5.93). This would seem to indicate that the steric effect of an angularly fused ring is larger than that of *o*-(*t*-butyl) group. Then one would expect 1-benzo[*c*]phenanthroic acid (LXVII, X = CO_2H, Y = H) to be still stronger. Rather surprisingly, this is found to be the weakest of the group (pK_a = 6.65). An apparent explanation would seem to be that here steric hindrance to solvation (acid weakening) has overcome steric hindrance to resonance (acid strengthening). The real reason may, however, be that, the ring system being no longer planar, the carboxyl group can enter into effective resonance with that part of the aromatic system which is coplanar with it. As a result, solvation and resonance effects acting cumulatively may weaken the acid considerably (449).

G. POLAROGRAPHIC REDUCTION

The electroreducibility (polarographic reduction) of any biaryl or arylalkene depends upon (a) the extent of conjugative interaction between the component fragments in the molecule and (b) the angle of twist (θ) between the component units. The effectiveness of adsorption of the substrate on the mercury cathode depends on the magnitude of θ. The smaller the value of θ (*i.e.*, the greater the planarity of the molecule), the greater is the ease of reduction. It is thus observed that the ease of reduction as revealed by the half-wave reduction potential ($-E_{1/2}$) is 2-phenylnaphthalene > 1-phenylnaphthalene; 2,2′-binaphthyl > 1,2′-binaphthyl > 1,1′-binaphthyl; 2-phenylanthracene > 1-phenylanthracene > 9-phenylanthracene (333). However, in the case of vinyl- and 2-cyclopentenylnaphthalenes, the 1 isomers are reduced more readily than the 2 isomers, indicating that steric effects are not significant in the 1 isomers. This is also indicated by a comparison of their ultraviolet absorption data.

Klemm and Kohlik (336) have determined the half-wave reduction potentials of a large number of alkyl-, alkylene-, and polymethylnaphthalenes. The values of $-\Delta E_{1/2}$ ($E_{1/2}$ for substituted naphthalene $- E_{1/2}$ for naphthalene) in millivolts have been determined experimentally and compared with values deduced empirically. These values for dimethylnaphthalenes are listed in Table XXIII.

The large discrepancy in $-\Delta E_{1/2}$ in the 1,8 and 2,3 derivatives is attributed to steric effects. Among the monoalkyl derivatives, the values of $-\Delta E_{1/2}$ for 1-(*t*-butyl)naphthalene is 56 while that for the 2 isomer is only 45. With smaller alkyl groups at the 1- and 2-positions, both 1- and 2-alkylnaphthalenes show close $-\Delta E_{1/2}$ values (1-Me, 21; 2-Me, 23; 1-Et, 33; 2-Et, 31; 1- or 2-*n*-propyl, 34; 1-allyl, 10; 2-allyl, 7). The $E_{1/2}$ value for 1-*t*-butylnaphthalene is 2.493 v as compared to 2.482 v for the 2 isomer, indicating greater difficulty in the electroreduction of the former.

H. CHROMATOGRAPHIC ADSORPTION

The degree of chromatographic adsorption is also affected by the planarity or otherwise of the organic compound: the more planar it is, the stronger it is adsorbed. Orchin and Reggel (464) have observed that chromatographic adsorption of 2,2′-binaphthyl on alumina is stronger than that of 1,2′-binaphthyl. This method has been employed with a set of 1- and 2-phenyl- and Δ^1-cyclohexenylnaphthalenes (330). Using a column of alumina, it is found that the 1 isomers are eluted first. The same observation is made of 1-phenyl-, cyclopentenyl-, or cyclohexenylnaphthalenes when they are run through a column packed with silicic acid impregnated with trinitrofluorenone or picric acid.

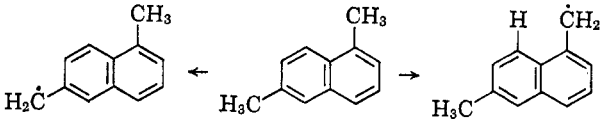
TABLE XXIII
DATA FOR POLAROGRAPHIC REDUCTION OF DIMETHYLNAPHTHALENES (336)

Dimethylnaphthalene	$-\Delta E_{1/2}$, mv Found	Calcd
1,2-	42	40
1,3-	46	40
1,4-	34	38
1,5-	38	38
1,6-	39	40
1,7-	32	40
1,8-	84	38
2,3-	64	42
2,6-	39	42
2,7-	48	42

A comprehensive investigation of the chromatographic adsorbabilities of several polycyclic aromatic hydrocarbons and their derivatives has been made (332). The results are found to be in harmony with the general principles and closely agree with the order arrived at from polarographic reduction. For example, in the increasing order of adsorption, 2-phenylanthracene > 1-phenylanthracene > 9-phenylanthracene; 2,2′-binaphthyl > 1,2′-binaphthyl > 1,1′-binaphthyl.

I. MISCELLANEOUS

Watts and Walker (571) have determined the emission spectra of several naphthylmethyl radicals derived from dimethylnaphthalenes. In symmetrically substituted derivatives such as 1,5-, 2,6-, or 2,3-dimethylnaphthalenes, the radicals formed from either of the methyl groups would be identical. In the case of those isomers containing both α- and β-methyl groups (*e.g.*, 1,2, 1,3, 1,6, and 1,7 isomers), two different methyl radicals may be obtained, involving either of the methyl

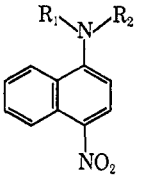


substituents. The ground-state vibrational frequencies of radicals derived from α-methyl group in naphthalene occur in the range 419–465 cm^{-1}; the corresponding range for the radicals derived from β-methyl group occurs around 518–520 cm^{-1}. This difference is at least in part due to the steric effect of *peri*-hydrogen affecting the planarity and hence conjugative stabilization of radicals derived from α-methyl substituents.

A spectacular illustration of *peri* effects is provided by a comparison of the melting points of 4-nitro-1-naphthylamine derivatives (20) (Table XXIV). Decrease of resonance between the 1,4 substituents considerably diminishes the polar character of the nitroamine and hence its melting point. It is assumed that crystal forces remain unaltered in these closely related compounds.

Strain energies of warped molecules have been studied by heat of combustion measurements (222). The difference in the heats of combustion ($\Delta\Delta H°$) between strained molecules and their totally unstrained isomers

TABLE XXIV
MELTING POINTS OF 4-NITRO-1-NAPHTHYLAMINES (20)



R_1	R_2	Mp, °C
H	H	191
CH_3	H	184
C_2H_5	H	176
$C_6H_5CH_2$	H	156
CH_3	CH_3	65
C_2H_5	C_2H_5	Liquid

may be considered as a measure of the strain energy (composed of intramolecular strain and crystal lattice energy defects due to nonplanarity). The $\Delta\Delta H°$ observed for dimethylphenanthrenes (between 2,7- and 4,5-dimethyl derivatives) is 12.6 kcal/mole and is taken as standard. The observed $\Delta\Delta H°$ with dimethylbenzo[*c*]phenanthrenes (between 5,8- and 1,12-dimethyl derivatives) is 11.6 kcal/mole, while the value for dimethyl-1,2-benzanthracenes (between 3′,6- and 1′,9-dimethyl derivatives) is 15.0 kcal/mole. The smaller $\Delta\Delta H°$ in the benzo[*c*]phenanthrene case would appear surprising in view of the inherent strain in this system. However, this observation may be reconciled in the following fashion: even in the parent system there is considerable steric strain, and introduction of further substituents at 1,12-positions does not cause much additional strain in contrast to the phenanthrene case. (It would perhaps be more appropriate to compare the heats of combustion of 1,12-dimethylbenzo[*c*]phenanthrene and its 3,10-dimethyl isomer. The 5,8-dimethyl derivative will still have two $CH_3\cdots H$ *peri* interactions. Such a comparison could probably make $\Delta\Delta H°$ a little larger, perhaps bringing it close to the phenanthrene value.) In the benzanthracene case the larger $\Delta\Delta H°$ is attributed to buttressing of the methyl groups by the fused rings in the overcrowded 1′,9-dimethyl derivative. More recently, 3,4,5,6- and 2,4,5,7-tetramethylphenanthrenes have been synthesized. Interesting results may be expected from thermochemical data on these compounds (440).

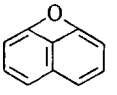
In naphthalenes *peri* interactions have been invoked to explain the observed partition behavior (466), refractive index (61), optical rotatory dispersion (322a), circular dichroism (98a), and electron spin resonance (213b, 549) of several derivatives.

III. CHEMICAL EVIDENCE FOR *peri* INTERACTION

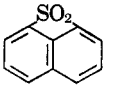
A. REACTIONS IN WHICH BOTH *peri* POSITIONS MAY BECOME INVOLVED

1. *peri* Cyclizations in Naphthalene Derivatives

A number of reactions are known in which the *peri* substituents in the naphthalene ring interact with each other or with an added reagent leading to the formation of a whole variety of ring systems across the *peri* positions. The *peri* ring so formed may be carbocyclic or heterocyclic, and the ring size varies from four-membered to eight-membered. There is only one report (33) of the formation of a four-membered ring. Dehydration of 1,8-dihydroxynaphthalene under nonoxidizing conditions is said to yield *peri*-monooxynaphthalene (LXXII). This is, however, subject to serious

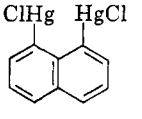


LXXII

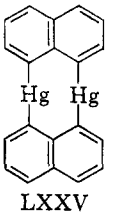


LXXIII

doubt in view of the inherent strain in such a molecule. More recently, the formation of the sulfone LXXIII has been reported (278a). Evidence has also been presented (278a, 483b) to indicate the possibility of 1,8-naphthyne being a reaction intermediate in the photolytic, thermal, and oxidative cleavage of some *peri*-naphtho compounds. For example, the formation of an ion of mass 126, presumably 1,8-naphthyne, has been observed in the mass spectrum of naphthalic anhydride. Pyrolytic reactions to form 1,8-naphthyne are also reported to be in progress (98a). The formation of eight-membered rings across the *peri* positions has been reported recently (58, 379, 380). The dimercury compound LXXV is formed in 94% yield when bis(1,8-



LXXIV

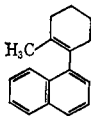
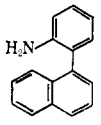


LXXV

chloromercury)naphthalene (LXXIV) is refluxed with sodium iodide in 95% ethanolic solution for 50 hr (380). The diketone XXXIII also contains an eight-membered *peri* ring. This is obtained by refluxing 1,8-dilithionaphthalene with acenaphthaquinone in ether for 6 hr followed by oxidation of the resulting diol with lead tetraacetate. While the diol is formed only in 14% yield, the oxidation proceeds smoothly to give the ketone in 81% (379).[5] The order of abundance of

(5) In this paper (379) the melting point of this ketone is reported to be >300°; no reference is however made to an earlier synthesis of this ketone by Knapp (340) who reports mp 350° dec. Knapp has also reported a few more derivatives of XXXIII.

TABLE XXV
ACENAPHTHENE DERIVATIVES OBTAINED BY *peri* CYCLIZATION

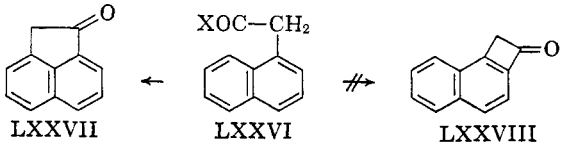
Starting compound	Conditions	Product	Yield, %	Ref
1,8-Bis(bromomethyl)naphthalene	PhLi–C_6H_6, 30 min at room temp, then reflux 1 hr	Acenaphthene	69	75
4-Bromo-1,8-bis(bromomethyl)-naphthalene	PhLi–C_6H_6, 30 min at room temp, then reflux 1 hr	5-Bromoacenaphthene	55	75
2,3-Benzo-1,8-bis(bromomethyl)-naphthalene	PhLi–C_6H_6, 1 hr at room temp	Aceanthrene	84	77
5,6-Bis(bromomethyl)acenaphthene	PhLi–C_6H_6, 45 min at 10°, 1 hr at room temp, 1 hr reflux	Pyracene	95	128
	(1) $AlCl_3$–CS_2, 0°, 6.5 hr (2) Se, 310–320°, 21 hr	Fluoranthene	Small	4
	(1) BCl_3–C_6H_6 (2) $AlCl_3$, 120° (3) HNO_2	Fluoranthene	Small	79

other *peri* rings is six-membered >> five-membered > seven-membered.

The several reactions leading to *peri* ring closure can be conveniently classified as follows: (a) the functional group at one *peri* position cyclizes into the other *peri* position which carries only hydrogen as the substituent; (b) both the *peri* substituents are different from hydrogen and react leading to ring closure; and (c) an added moiety becomes part of the new ring formed. Under type (a) fall the innumerable intramolecular cyclizations involving carboxylic acids and their derivatives such as acid chlorides and esters under Friedel–Craft conditions. Type (b) ring closures lead to naphthostyrils, naphthotriazines, sultones, sultams, and several other heterocyclic rings. A large number of type (c) reactions are known leading to perimidines. An account of such *peri* cyclizations resulting in carbocyclic derivatives is presented below. Heterocyclic structures formed in this way are discussed later in this section. The formation of sultams and sultones of this series are not considered here, as these have been reviewed earlier (433).

a. Acenaphthene Derivatives

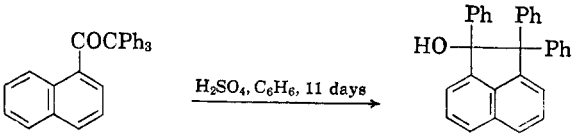
The cyclization of 1-naphthylacetic acid derivatives (LXXVI) appears to occur exclusively to the *peri* position giving acenaphthenones (LXXVII). The alternate 1,2 cyclization would lead to a severely strained four-membered ring (LXXVIII). Examples of the latter type do not seem to have been recorded so far. Indeed an early observation has been made (572) recording the failure of phenylacetyl chloride and benzoyl chloride



LXXVII LXXVI LXXVIII

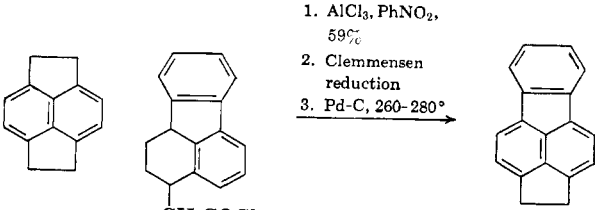
to cyclize intramolecularly under Friedel–Crafts conditions; this would then suggest that formation of fused ring systems containing three- and four-membered rings is difficult, if not impossible. Table XXV summarizes the results of several investigations in which acenaphthene derivatives are formed by *peri* cyclization of appropriate naphthalene derivatives.

Acenaphthene itself is obtained in 69% yield by refluxing 1,8-bis(bromomethyl)naphthalene with phenyllithium in benzene solution. A similar reaction with 4-bromo-1,8-bis(bromomethyl)naphthalene yields 5-bromoacenaphthene (55%) (75). The migration of a phenyl group followed by 1,8 ring closure gives (432) 1,2,2-triphenylacenaphthenol (LXXX) from 1-naphthyl trityl ketone (LXXIX).



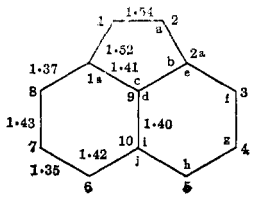
LXXIX LXXX

Until recently, it was believed difficult to bridge both pairs of the *peri*-carbon atoms through five-membered rings. Thus a number of earlier attempts to synthesize structure LXXXI met with failure (202, 215, 384, 385, 412). In the synthesis of the related compound LXXXIII (338), while *peri* cyclization was possible



LXXXI LXXXII LXXXIII

with the partially hydrogenated derivative LXXXII, the fully aromatic system (3-fluoranthenylacetyl chloride) failed to undergo the reaction and thus had to be prepared by dehydrogenation of its partially saturated analog. Attempts to cyclize 5-acenaphthylacetyl chloride to the carbonyl derivative of LXXXI using stannic chloride, anhydrous aluminum chloride, or a mixture of aluminum chloride–sodium chloride also did not succeed (338). This marked resistance for the formation of a second five-membered *peri* ring is interesting since a second *peri* ring with six or seven members is easily formed; it would then appear that the size of the second *peri* ring is an important criterion in ease of closure. This may be interpreted to be due to a possibly increased distance between the 5- and 6-positions of acenaphthene as compared to the distance between the *peri* positions in naphthalene itself. This is borne out by a consideration of the bond angles and bond distances in acenaphthene (LXXXIV). The large dif-

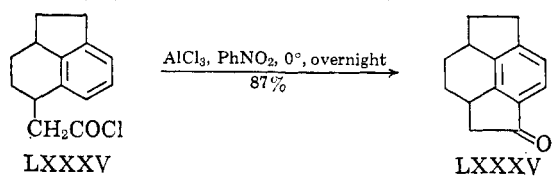


LXXXIV

a = 105.2°, f = 118.4°
b = 108.6°, g = 121.9°
c = 112.4°, h = 121.5°
d = 123.8°, i = 115.8°
e = 118.6°, j = 128.4°

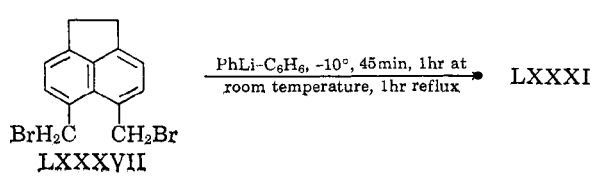
ference between $\angle C_5C_{10}C_6$ (= 128.4°) and $\angle C_{1a}C_9C_{2a}$ (= 112.4°) indicates a clear and significant distortion of the molecular arrangement and is attributable to the pulling together of the *peri*-carbon atoms at one end by the dimethylene bridge. In contrast, in naphthalene, as a result of symmetry, these angles do not differ from 120°. If, as a consequence of this distortion, the distance between the 5- and 6-positions in acenaphthene increases to a value that is outside the maximum possible distance for the formation of a five-membered ring, then *peri* ring closure would be prevented.

Acid chloride LXXXV has been cyclized to tetrahydropyracenone (LXXXVI) in similar fashion as LXXXII (11). Of greater interest, however, is the



LXXXV LXXXVI

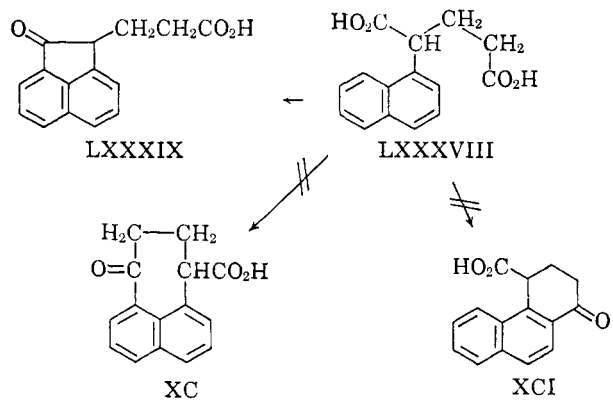
recent synthesis of pyracene itself by Carpino and Gowecke (128) who succeeded in cyclizing the bis-(bromomethyl) precursor in high yield by means of phenyllithium.



LXXXVII LXXXI

The cyclization of substituted 1-naphthylacetyl chlorides seems to be a convenient method for the preparation of acenaphthenones as shown by the large number of reactions collected in Table XXVI. However, Green and Hey (243) have found that the presence of a 4- or 6-methoxy group in the naphthalene ring prevents the *peri* cyclization of 1-naphthylacetic acid. The 5- and 7-methoxy acids do cyclize. The failure of the 6-methoxy acid is attributed to insufficient activation of the *peri* position by the methoxyl; the case with the 4-methoxy isomer is less easy to explain.

When there is a choice between the formation of a five- or seven-membered 1,8 ring and a six-membered 1,2 ring in naphthalene, the five-membered *peri* ring is seen to be favored. One may expect α-(1-naphthyl)-glutaric acid (LXXXVIII) to yield either the *peri*-cyclized product LXXXIX (acenaphthenone) or XC (homophenalanone) or the 1,2-cyclized product XCI (ketophenanthrene). Ansell and Hey (16) investigated this reaction and isolated only LXXXIX as the prod-



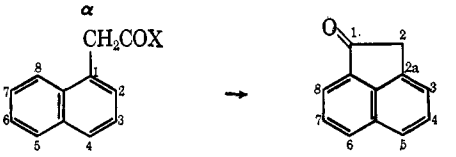
LXXXIX LXXXVIII XC XCI

uct. An investigation of the cyclization behavior of 1-naphthylsuccinic acid may be expected to throw light on the competitive formation of a five- or six-membered *peri* ring; this does not seem to have been made so far.

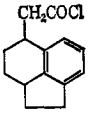
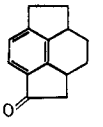
b. Phenalene Derivatives

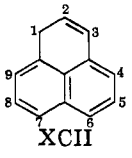
The remarkable ease with which six-membered rings are formed has made possible the synthesis of phenalene derivatives (XCII) by *peri* ring closure of suitable naphthalene compounds (Table XXVII). The often employed reaction is the intramolecular Friedel–Crafts reaction of β-(1-naphthyl)propionic acids and their derivatives (XCIII). The reaction may lead to a phenalenone (XCV), 2,3-dihydrophenalenone (XCIV), or 4,5-benzindanone (XCVI), depending upon the reaction conditions and the starting compound. Occasionally it is possible to get one of these products exclusively by suitable choice of experimental conditions, though more often only a mixture is obtained. Many instances are on record (15, 206, 209, 486) where an earlier claim of having obtained any one of these ketones as a single product is shown to be erroneous. The products really consisted of a mixture of two, or all of the three ke-

TABLE XXVI
ACENAPHTHENONES BY *peri* CYCLIZATION

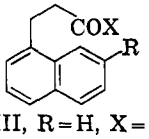


a b

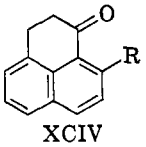
Starting compound	Conditions	Product (b)	Yield, %	Ref
a, X = OH				
Unsubstituted	PPA, 60–100°, 30 min	Unsubstituted	40	243
1,2,3,4-Tetrahydro	HF, room temp, 20 hr	2a,3,4,5-Tetrahydro	74	304
2-Methoxy	HF, room temp, 20 hr	3-Methoxy	96	304
	PPA, 60–100°, 30 min	3-Methoxy	30	243
5-Methoxy	PPA, 60–100°, 30 min	6-Methoxy	25	243
7-Methoxy	PPA, 60–100°, 30 min	8-Methoxy	30	243
7-Methoxy-1,2,3,4-tetrahydro	HF, room temp, 20 hr	8-Methoxy-2a,3,4,5-tetrahydro	96	304
a, X = Cl				
Unsubstituted	$AlCl_3$–CS_2 or	Unsubstituted	82	223
	$AlCl_3$–$PhNO_2$	Unsubstituted	82	223
	$AlCl_3$–C_6H_6	Unsubstituted	20	243
1,2,3,4-Tetrahydro	$AlCl_3$–CS_2	2a,3,4,5-Tetrahydro	60	97
2-Ethyl	$AlCl_3$–C_6H_6, 1 hr, room temp	3-Ethyl	85	39
2,6-Dimethyl	$AlCl_3$–$PhNO_2$	3,7-Dimethyl	...	118
2,7-Dimethyl	$AlCl_3$–$PhNO_2$	3,8-Dimethyl	...	118
4-Bromo	$AlCl_3$–$PhNO_2$, 80–90°	5-Bromo	...	413
5-Methoxy	$AlCl_3$–C_6H_6	6-Methoxy	25	243
1,2,3,4-Tetrahydro-4,5-(*o*-phenylene)	$AlCl_3$–$PhNO_2$	2a,3,4,5-Tetrahydro-5,6-(*o*-phenylene)	59	338
α-Phenyl	$AlCl_3$–C_6H_6	2-Phenyl	60	343
α,α-Diphenyl	$AlCl_3$–C_6H_6, 15 hr	2-Phenyl	40	416
α,α-Diphenyl	$SnCl_4$, steam bath	2,2-Diphenyl	...	36
α,α-Di(*p*-biphenylyl)	$SnCl_4$, steam bath	2,2-Di(biphenylyl)	...	36
	$AlCl_3$–$PhNO_2$, 0°, overnight		87	11



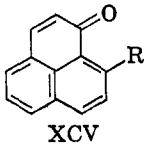
XCII



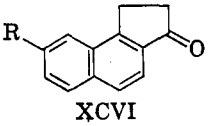
XCIII, R = H, X = OH, Cl, OC_2H_5



XCIV



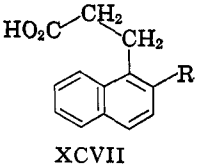
XCV



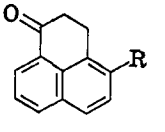
XCVI

tones. The course of the reaction is considerably influenced by the cyclizing conditions employed. For example, the use of polyphosphoric acid (PPA) in the cyclization of β-(7-alkyl-1-naphthyl)propionic acid (XCIII, X = OH, R = alkyl) at 140° for 45 min resulted in the formation of mainly the phenalenone (XCV, R = alkyl); the use of the same reagent at a slightly lower temperature and for a shorter reaction time (110°, 15 min) caused the formation of dihydrophenalenone (XCIV, R = alkyl). The formation of phenalenone is shown to be due to dehydrogenation of the initially formed dihydro compound by PPA (580).

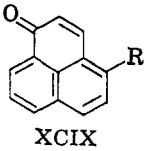
The nature of the condensing agent also profoundly affects the course of the reaction. This may be illustrated by considering the products obtained from β-(2-methoxy-1-naphthyl)propionic acid (XCVII, R = OMe). Use of phosphorus pentoxide (45) afforded the



XCVII



XCVIII

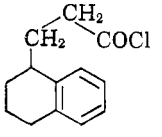


XCIX

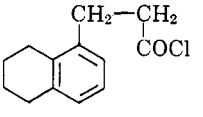
phenalenone (XCIX, R = OMe) while with hydrogen fluoride (45, 486) the dihydrophenalenone (XCVIII, R = OMe) is the main product. A minor amount of XCV (R = H) was also isolated (45) by the action of phosphorus pentoxide on XCVII (R = OCH_3). With the unsubstituted acid itself (XCVII, R = H) using hydrogen fluoride as the condensing agent, Fieser and Gates (208) isolated XCVIII (R = H) in 81% yield

with minor amounts of 4,5-benzindanone (XCVI). When stannic chloride or aluminum chloride was used in place of hydrogen fluoride, in addition to the above products, a considerable amount (40%) of phenalenone (XCIX, R = H) was also obtained (139, 208).

The direction of cyclization, whether *peri* or 1,2 cyclization, is dependent on the nature of the starting compound; the position and nature of substituents when present in the naphthalene ring also determine the mode of cyclization. Thus the acid chloride C containing the side chain in the reduced naphthalene ring undergoes smooth *peri* cyclization (97); on the other hand, CI carrying the side chain in the aromatic portion 1,2-cyclizes (401) of necessity.



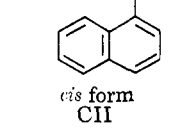
C



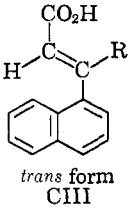
CI

The steric and electronic effects of substituents, particularly alkyl and methoxyl, have been fairly well investigated (45, 243, 486). The cyclization of 2-, 5-, and 7-methoxy- and 2,6-dimethoxy-1-naphthylpropionic acids gave the *peri* ketone in each case. The 6-methoxy isomer gave only the 1,2-cyclized product, a result comparable to that with 6-methoxy-1-naphthylacetic acid (86, 243); presumably here also, the *peri* position is not sufficiently activated and possibly deactivated by the 6-methoxyl to force *peri* cyclization. The results on the cyclization of a series of β-(7-alkyl-1-naphthyl)propionic acids (XCIII, X = OH, R = Me, Et, *i*-Pr, and *t*-Bu) provide an interesting contrast; 1,8 cyclization proceeds quite satisfactorily when the 7-alkyl group is methyl, ethyl, or even isopropyl, but, when R = *t*-butyl, the milder conditions used for acids containing the smaller alkyl groups cannot bring about the reaction. When the reaction is forced by employing drastic conditions, the *peri* ring closure does occur but not before the bulky *t*-butyl group is lost (243).

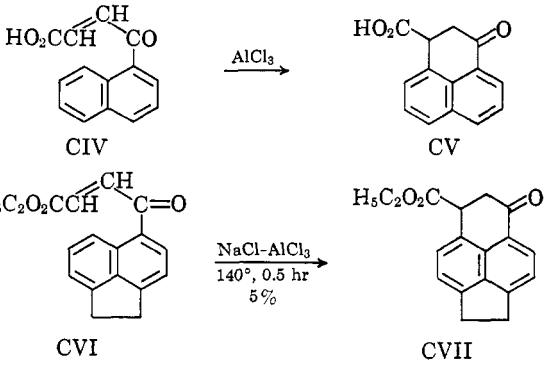
An unfavorable configuration also sometimes precludes 1,8 ring closure. Thus, the *cis* form (mp 145°) of β-1-naphthylacrylic acid (CII, R = H) cyclizes readily with concentrated sulfuric acid or hydrogen fluoride to the phenalenone, but the *trans* isomer (CIII, R = H) (mp 211°) does not (386). Indeed the configurational assignments in this series were arrived at from a study of cyclization behavior. Similarly *cis*-β-(1-naphthyl)-β-(*o*-bromophenyl)acrylic acid (CII, R = *o*-C_6H_4Br) undergoes *peri* cyclization, but the *trans* isomer does not (471). In these cases, phenalenones are obtained directly by the ring closure of appropriate naphthalene derivatives containing an unsaturated side chain at the 1-position. Data on a number of such syntheses are presented in Table XXVIII. An



cis form
CII



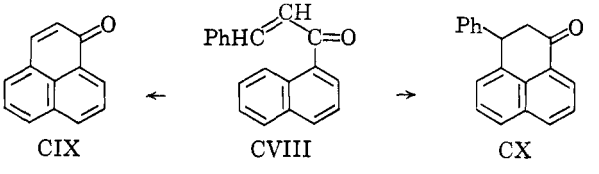
trans form
CIII



CIV CV CVI CVII

examination of these data indicates that in a few cases, the cyclizations occur *via* intramolecular addition of the aromatic moiety to the double bond of the unsaturated side chain (117, 202, 560) rather than by simple dehydration or dehydrohalogenation.

The loss of a substituent during *peri*-cyclization has been reported, *e.g.*, bromine, methoxyl or *t*-butyl from the aromatic ring (413, 581) or a terminal phenyl group (117,344). The latter seems to occur with 1-cinnamoylnaphthalenes; there is, however, a patent claim describing the cyclization of 1-cinnamoylnaphthalene without loss of the phenyl group (292).



CIX CVIII CX

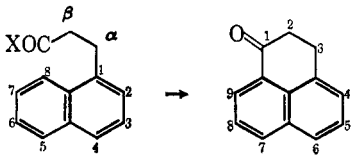
In polynuclear aromatic ketones, hydrogen atoms situated *peri* to the carbonyl are rendered labile by the action of aluminum chloride at higher temperatures to permit *peri* cyclization (Scholl's reaction). Reviews of this type of reaction covering the literature up to 1953 are available (254, 539). This reaction has been applied among others, to 1-(1′-naphthoyl)-4-methylnaphthalene (114) and 2-phenanthryl 1-methyl-4-naphthyl ketone (115). Since the ring systems involved are much more complex than naphthalene, it is not intended to cover them here.

Other reactions leading to phenalene derivatives are collected in Table XXIX.

c. Homophenalene Derivatives

The *peri* cyclization of γ-(1-naphthyl)butyric acid (CXI, $R_1 = R_2 = H$) and its derivatives leads to homophenalenes (CXII). As with the naphthylpropionic acids discussed earlier, the alternate ring closure to give CXIII also takes place in some cases. The latter

TABLE XXVII
2,3-DIHYDROPHENALENE DERIVATIVES

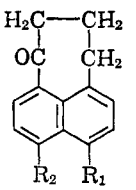


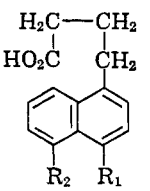
Starting compound	Conditions	Product	Yield, %	Ref
X = OH				
Unsubstituted	HF, room temp, 2.5 hr	Unsubstituted[d]	81	208
	$SnCl_4$, 120°, 3 hr	Unsubstituted[a]	...	139
2-Methyl	HF, room temp, 2.5 hr	4-Methyl	98	93
4-Methyl	HF, room temp, 2.5 hr	6-Methyl	82	93
7-Methyl (also ethyl, isopropyl)	PPA, 140°, 45 min	Not formed[b]	...	580
	PPA, 110–120°, 15 min	9-Alkyl	Mainly	580
	HF	9-Alkyl[b]	87–94	580
2-Methoxy	HF, room temp, 3.5 hr	4-Methoxy	80	45
	P_2O_5–C_6H_6, water bath, 2 hr	4-Methoxy[c]	Trace	45
	P_2O_5, water bath, 2 hr	4 Methoxy	Small	59
	HF	4-Methoxy	Mainly	486
5-Methoxy	PPA, 60–100°, 30 min	7-Methoxy	60	243
	85% H_2SO_4, 100°	7-Methoxy	80	243
7-Methoxy	PPA, 60–100°, 30 min	9-Methoxy	16	243
	85%, H_2SO_4, 100°	9-Methoxy	20	243
2,6-Dimethoxy	HF	4,8-Dimethoxy[d]	High	486
4,5-Dimethylene	HF	6,7-Dimethylene	...	209
	HF	6,7-Dimethylene[e]	...	486
4,5-Trimethylene	HF, 0°, 10 hr	6,7-Trimethylene	80	385
4-(β-Carboxyethyl)	HF, 0°, overnight	6-(β-Carboxyethyl)	...	385
5-(β-Carboxyethyl)	HF, 15 hr	7-(β-Carboxyethyl)	73	384
X = Cl				
Unsubstituted	$AlCl_3$	Unsubstituted[f]	...	139
	$AlCl_3$–$PhNO_2$	Unsubstituted[f]	...	15
	$AlCl_3$–C_6H_6, 0°, 2 hr	Unsubstituted	...	119
	$AlCl_3$–ligroin, heated 1.5 hr	Unsubstituted	30	413
2-Methyl	$AlCl_3$–light petroleum	4-Methyl[f]	65	339
4-Methyl	$AlCl_3$–$PhNO_2$	6-Methyl	90	117
7-Alkyl (Me, Et, or *i*-Pr)	$AlCl_3$–$C_2H_4Cl_2$, 15°	9-Alkyl	74–96	580
	$AlCl_3$–$PhNO_2$	9-Alkyl	57–81	580
	$SnCl_4$	9-Alkyl[d]	90–93	580
2,6-Dimethyl	$AlCl_3$–$PhNO_2$	4,8-Dimethyl	...	118
2,7-Dimethyl	$AlCl_3$–$PhNO_2$	4,9-Dimethyl	...	118
2-Methoxy	$SnCl_4$–C_6H_6	4-Methoxy	80	45
4-Methoxy	$AlCl_3$–ligroin, water bath	Unsubstituted	Trace	413
5-Methoxy	$SnCl_4$–C_6H_6, 0°, 2 hr	7-Methoxy	70	243
5,6-*o*-Phenylene	$AlCl_3$–$PhNO_2$, 0°, 20 hr	7,8-*o*-Phenylene[d]	25	37
4-Bromo	$AlCl_3$–ligroin, water bath	Unsubstituted[g]	6	413
1,2,3,4-Tetrahydro	$AlCl_3$–CS_2	3a,4,5,6-Tetrahydro	60	97
5,6,7,8-Tetrahydro	$AlCl_3$–C_6H_6, 18 hr at room temp, 0.5 hr at 35°	...[h]	...	401
X = OH				
α-Methyl	HF, room temp, 24 hr	2-Methyl	96	206
	HF or $AlCl_3$	2-Methyl[d]	60	15
α-Ethyl	HF	2-Ethyl	60	15
	$AlCl_3$–ligroin, heat 2 hr	2-Ethyl	90	413
α-*n*-Propyl	HF	2-*n*-Propyl[d]	65	15
α-*n*-Butyl	HF	2-*n*-Butyl[d]	8	15
β-Methyl	HF, room temp, 3 hr	3-Methyl	87	93
	HF, 10°, 1 hr	3-Methyl[f]	86	386
	HF, room temp, 24 hr	3-Methyl[d]	75	17
β-Ethyl	HF, room temp, 24 hr	3-Ethyl[e]	40	17
β-*n*-Propyl	HF, room temp, 24 hr	3-*n*-Propyl[e]	25	17
β-*n*-Butyl	HF, room temp, 24 hr	3-*n*-Butyl[e]	70	17

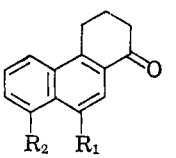
TABLE XXVII (*Continued*)

Starting compound	Conditions	Product	Yield, %	Ref
β-Hydroxy-β-phenyl	Cold H_2SO_4	...[i]	...	344
Ethyl ester of the above	H_2SO_4, room temp, 2 hr	...[i]	...	344
X = Cl				
α,α-Dimethyl	$AlCl_3$–$PhNO_2$, 0°	2,2-Dimethyl	...	119
α-Ethyl	$AlCl_3$–ligroin, water bath, 2 hr	2-Ethyl	95	413
β-Phenyl	$AlCl_3$	3-Phenyl	...	291
β-Phenyl-2-methoxy	$AlCl_3$–C_6H_6	3-Phenyl-4-methoxy	Good	342

[a] 1,2-Cyclization product, 4%; phenalenone, 40%. There seems to be considerable dehydrogenation. [b] Phenalenone is the only product isolated. With HF, a trace of phenalenone is also formed. [c] 4-Methoxyphenalenone is the major product. Unsubstituted phenalenone itself is also obtained. [d] A small yield of 1,2-cyclized product is also obtained. [e] The unsaturated phenalenone and some 1,2-cyclized product are also formed. [f] Some phenalenone is also formed. [g] Loss of bromine during reaction. [h] 70% of 1,2-cyclized product. [i] 35% yield of 3-phenylphenalenone is obtained.


CXII

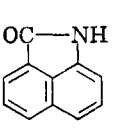

CXI

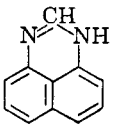

CXIII

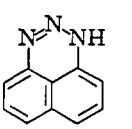
type of ring closure seems to be particularly favored if the side chain is derived from a dicarboxylic acid (16, 243). In the case of γ-(4-methoxy-1-naphthyl)butyric acid (CXI, R_1 = OCH_3; R_2 = H), instead of the expected 1,8 product, the 1,2 product is reported (38, 243, 346). The action of aluminum chloride on γ-(5-methoxy-1-naphthyl)butyric acid (CXI, R_1 = H; R_2 = OMe) is said (346, 347) to give dihydrohomophenalenone (CXII), whereas the use of stannic chloride affords ketophenanthrene (CXIII). Lockett and Short (387) reported only *peri* products from either method. Their observations are supported by subsequent work (243). The preferential formation of a seven-membered *peri* ring over an energetically more favored six-membered one across 1,2-positions is rationalized by considering the activation at the *peri* position by the 5-methoxyl which appears to be just sufficient to overcome the strain in forming a seven-membered ring. Tables XXX and XXXI list examples of *peri* and 1,2 cyclizations of naphthylbutyric acids.

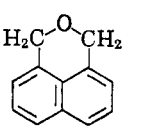
d. Heterocyclic Derivatives.

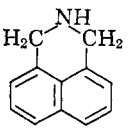
The synthesis of a large number of heterocyclic compounds with *peri*-bridged naphthalene rings has been reported. These are widely scattered in the literature, but an attempt is made here to collect most of the more pertinent references on such compounds. The ease of *peri* cyclization has led to the synthesis of diverse ring systems some of which are indicated below: naphthostyril (CXIV), perimidine (CXV), naphthotriazines (CXVI), 1H,3H-naphtho[1,8-*cd*]pyran(CXVII), 1H,-2H,3H-naphtho[1,8-*cd*]pyridine (CXVIII), naphth-[1,8-*de*]oxazine (CXIX), 2H,3H-naphtho[1,8*bc*]thiopyran (CXX), naphtho[1,8-*ef*][1,4]diazepine (CXXI).

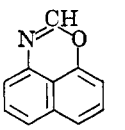

CXIV

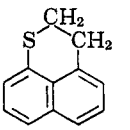

CXV

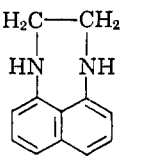

CXVI


CXVII

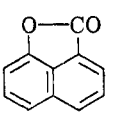

CXVIII

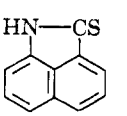

CXIX


CXX


CXXI

Naphthostyrils can be prepared by the following reactions: (i) heating ethanolic solutions of 8-amino-1-naphthoic acids, (ii) reduction of 8-nitro-1-naphthoic acids which may lead to simultaneous ring closure, and (iii) heating a *peri*-halonaphthoic acid with ammonia under pressure. A wide variety of suitable modifications of these methods have been successfully employed in the preparation of these derivatives. Data concerning the naphthostyrils are collected in Table XXXII. The ease of formation of naphthostyril from 8-amino-1-naphthoic acid may be contrasted with the nonformation of the lactam from 1,2-, 2,1-, and 2,3-aminonaphthoic acids. This is possibly due to the excessive strain involved in the formation of a four-membered ring. Presumably for the same reason, the lactone CXXII of 8-hydroxy-1-naphthoic acid is known, whereas similar


CXXII


CXXIII

lactonization does not seem to have been realized in 1,2-, 2,1-, and 2,3-hydroxynaphthoic acids (172).

It is also of interest to note that the cyclization of 1-naphthyl isothiocyanate has been carried out (167) to give thionaphthostyril (CXXIII); the related conversion of 1-naphthyl isocyanate to naphthostyril does not seem to have been accomplished.

TABLE XXVIII
peri CYCLIZATIONS OF UNSATURATED SIDE CHAINS

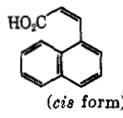
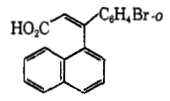
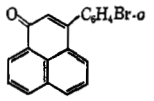
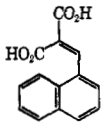
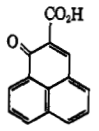
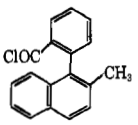
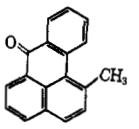
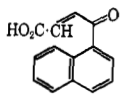
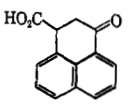
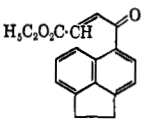
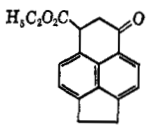
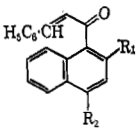
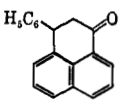
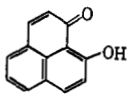
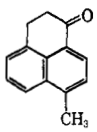
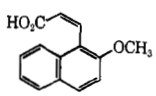
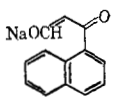
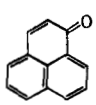
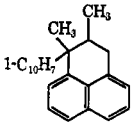
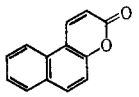
Starting compound	Conditions	Product	Yield, %	Ref
 (*cis* form)	HF, 1 hr		82	386
 (or the methyl ester)	HF		33	471
	HF, 0°		87	386
	$AlCl_3$		Quant	43
	$AlCl_3$		...[a]	289
	$NaCl–AlCl_3$, 140°, 0.5 hr		5[a]	202
 $R_1 = R_2 = H$	$AlCl_3–CS_2$, 30–35°		...[a]	292
	$AlCl_3–CS_2$, 2 hr		25[b]	344
$R_1 = OCH_3; R_2 = H$	$AlCl_3–C_6H_6$, 25 min, reflux		45[c]	344
$R_1 = H; R_2 = CH_3$	$AlCl_3–C_6H_6$		...[d]	117
	$P_2O_5–C_6H_6$ PCl_5	. . . . . .	...[e] ...[e]	59 59
	82% $H_2SO_4–CCl_4$, 30 min		64	381

TABLE XXVIII (*Continued*)

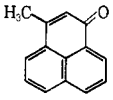
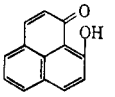
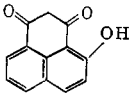
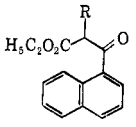
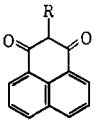
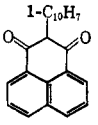
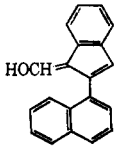
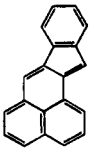
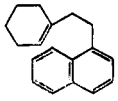
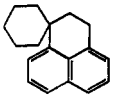
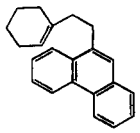
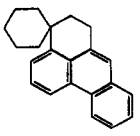
Starting compound	Conditions	Product	Yield, %	Ref
	Polymerize slowly in presence of 25% Floridin or heat with $(PhCO)_2O_2$ at 100°		...	594

[a] Intramolecular addition. [b] Loss of terminal phenyl group. [c] Loss of terminal phenyl group and demethylation. [d] Loss of terminal phenyl group. Saturated side chain is formed. [e] 1,2-Cyclization occurs to give the lactone



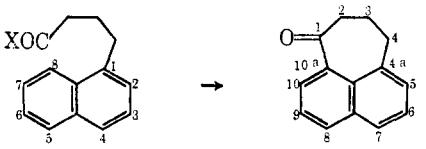
No *peri* cyclization. Use of P_2O_5–C_6H_6 results in smaller yields of the lactone. Large amounts of the lactone formed with PCl_5.

TABLE XXIX
MISCELLANEOUS REACTIONS LEADING TO PHENALENE DERIVATIVES

Starting compound	Conditions	Product	Yield, %	Ref
1,8-Diacetylnaphthalene	Piperidine		...	150
2-Ethoxy-1,8-diacetylnaphthalene	84% H_2SO_4, 5–16°, 4 hr		77[a]	516
2-Methoxy-1-naphthoylacetyl chloride	$AlCl_3$, $PhNO_2$		31	90
	Concd H_2SO_4, 80°			
R = H		R = H	Quant	591
R = Me		R = Me	35[b]	591
R = Et		R = Et	50[b]	591
1,8-Naphthalic acid	$1\text{-}C_{10}H_7CH_2CO_2H$, anhydrous NaOAc, 220–240°, 4 hr		82	418
	93% H_2SO_4, C_6H_6		18	7
	$AlCl_3$–CS_2, ice, 7 hr		55	139
	$AlCl_3$–CS_2, ice, 7 hr		80	269

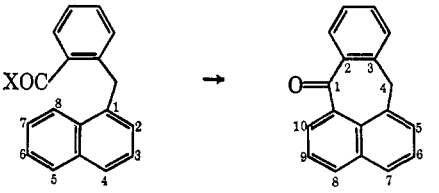
[a] Dealkylation also takes place. [b] 1,2-Cyclized product is also formed in 40–45%.

TABLE XXX
HOMOPHENALENE DERIVATIVES BY *peri* CYCLIZATION

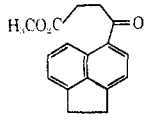
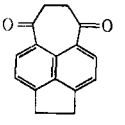
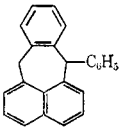


a b

Starting compound	Conditions	Product (b)	Yield, %	Ref
a, X = OH				
5-Methoxy	$AlCl_3$	8-Methoxy	Good	347
	$SnCl_4$–$C_6H_5CH_3$	...	...[a]	347
	$AlCl_3$ or $SnCl_4$	8-Methoxy	...	387
	85% H_2SO_4 or $SnCl_4$	8-Methoxy	35	243
	PPA	8-Methoxy	50	243
1,2,3,4-Tetrahydro	$AlCl_3$–CS_2	4a,5,6,7-Tetrahydro	12	98
a, X = Cl				
2-Methoxy	$SnCl_4$–C_6H_6, 15 min	5-Methoxy	94	236
7-Methoxy	$SnCl_4$, low temp	10-Methoxy	19[b]	236
7-Methoxy-1,2,3,4-tetrahydro	$SnCl_4$, low temp	10-Methoxy-4a,5,6,7-tetrahydro	90	236
1,2,3,4-Tetrahydro	$AlCl_3$–CS_2	4a,5,6,7-Tetrahydro	Low	237
	$SnCl_4$–C_6H_6, 48 hr	...	Nil	237
	$AlCl_3$–$PhNO_2$, room temp for 3 days, water bath, 6 hr	4a,5,6,7-Tetrahydro	29	237
	HF, overnight	4a,5,6,7-Tetrahydro	Very small	237
	P_2O_5–H_3PO_4, 95°, 10 min	4a,5,6,7-Tetrahydro	88	237



c d

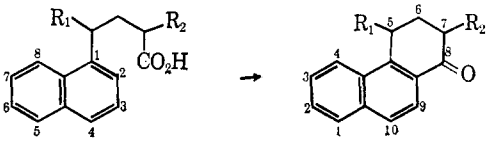
Product (d)				
c, X = OH				
2,6-Dimethyl-4-methoxy	82% H_2SO_4, water bath, 10 min	5,9-Dimethyl-7-methoxy	90	200
2,7-Dimethoxy	82% H_2SO_4, heat	5,10-Dimethoxy	90	200
c, X = Cl				
2-Methyl	$AlCl_3$–$PhNO_2$, 0°, 2 hr	5-Methyl	75–85	201
2,3-Dimethyl	$AlCl_3$–$PhNO_2$, 0°, 2 hr	5,6-Dimethyl	75–85	201
2,6-Dimethyl	$AlCl_3$–$PhNO_2$, 0°, 2 hr	5,9-Dimethyl	75–85	201
2,7-Dimethyl	$AlCl_3$–$PhNO_2$, 0°, 2 hr	5,10-Dimethyl	75–85	201
2-Methoxy	$AlCl_3$–$PhNO_2$, 0 ', 2 hr	5-Methoxy	75–85	201
	$NaCl$–$AlCl_3$, 150°, 1 hr		43	202
8-Benzyhydryl-1-hydroxy-methylnaphthalene	HCO_2H or CH_3CO_2H containing trace of H_2SO_4, steam bath		100	360

[a] Only 1,2-product is obtained. [b] The major product (78%) is obtained by 1,2 ring closure.

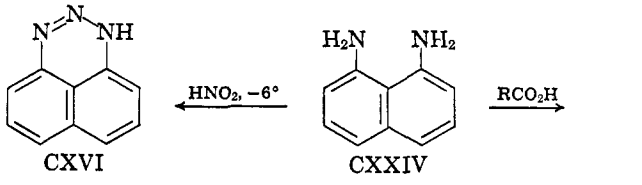
Perimidines are obtained in fair yield when 1,8-naphthalenediamine (CXXIV) and its derivatives are heated with aliphatic or aromatic acids or their derivatives. In Table XXXIII are given data on the synthesis of perimidines.

The triazines CXVI result by the action of nitrous acid on *peri*-diamines at low temperatures (6, 475, 563). Table XXXIV lists the *peri*-naphthotriazines that have been prepared. The *peri*-diamines react with remarkable readiness with a variety of reagents participating

TABLE XXXI
1,2 CYCLIZATION OF γ-(1-NAPHTHYL)BUTYRIC ACIDS

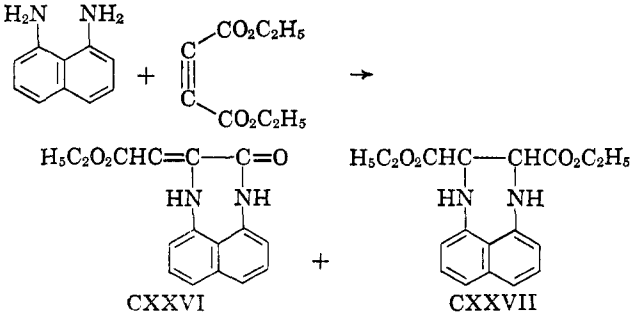


Starting compound	Conditions	Product	Yield, %	Ref
$R_1 = R_2 = H$, 4-OCH_3	85% H_2SO_4, 100°	$R_1 = R_2 = H$, 10-OCH_3	50	243
Acid chloride of the above	$SnCl_4$–C_6H_6	$R_1 = R_2 = H$, 10-OCH_3	92	38
Acid chloride of the above	$AlCl_3$–$C_2H_2Cl_4$, ice, 16 hr	$R_1 = R_2 = H$, 10-OCH_3	80	346
$R_1 = R_2 = H$, 5-OCH_3	$SnCl_4$–C_6H_6	$R_1 = R_2 = H$, 1-OCH_3	40	346
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 4-OCH_3	85% H_2SO_4, 100°, 2 hr	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 10-OCH_3	80	243
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 4-OCH_3	$SnCl_4$–C_6H_6	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 10-OCH_3	50	243
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 5-OCH_3	85% H_2SO_4, 100°	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 1-OCH_3	90	243
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 6-OCH_3	85% H_2SO_4, 100°	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 2-OCH_3	90	243
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 6-OCH_3	PPA, 60–100°, 30 min	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 2-OCH_3	70	343
Acid chloride of above	$SnCl_4$–C_6H_6, 0°, 2 hr	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 2-OCH_3	90	243
$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 7-OCH_3	85% H_2SO_4, 100°	$R_1 = H$, $R_2 = CH_2CH_2CO_2H$, 3-OCH_3	90	243
$R_1 = CO_2H$, $R_2 = H$	HF, 24 hr	$R_1 = CO_2H$, $R_2 = H$	95	16



CXVI CXXIV CXXV

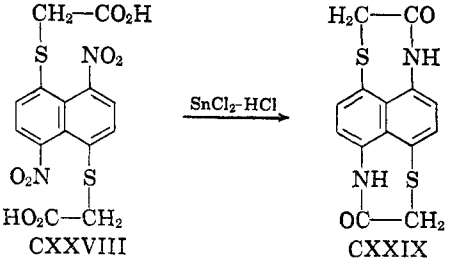
in both addition and condensation reactions. This led Sachs (505) to refer them as "ultra-orthodiamines." For example, 1,8-naphthalenediamine reacts (296) with acetylenedicarboxylic ester in ethanolic solution furnishing 13% of the condensation–addition product CXXVI and 41% of addition product CXXVII. The latter is also obtained by heating the 1,8-diamine with diethyl α,β-dibromosuccinate in pyridine for 2 hr (296).



CXXVI CXXVII

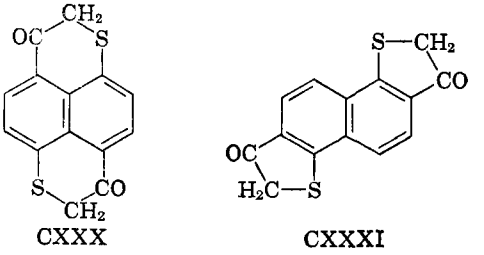
A number of derivatives with sulfur in the *peri* ring have been prepared (Table XXXV). Interesting cases of double *peri* cyclizations are reported in this series.

Prolonged treatment of 4,8-dinitro-1,5-naphthalenebis-(thioglycollic) acid(CXXVIII) with stannous chloride and hydrochloric acid gives CXXIX (365). Treatment of 1,5-naphthalenebis(thioglycollic) acid itself (CXXVIII, with H instead of NO_2) first with PCl_5 and then



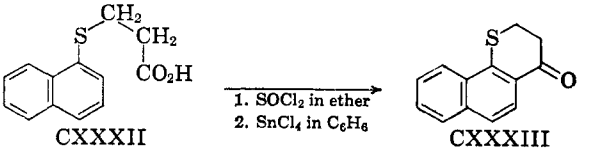
CXXVIII CXXIX

with aluminum chloride in carbon disulfide leads to the doubly *peri*-cyclized ketone (CXXX) together with larger amounts of the 1,2-cyclized product (CXXXI) (123, 365). In this connection it is of interest that cycli-



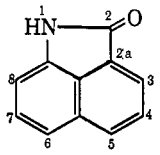
CXXX CXXXI

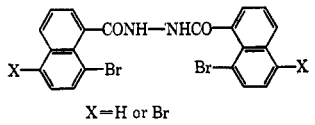
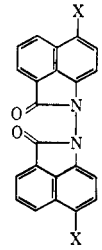
zation of β-(1-naphthylthio)propionic acid (CXXXII) with stannic chloride in benzene solution entirely took place in the 1,2 direction (365). Data relating to the



CXXXII CXXXIII

TABLE XXXII
NAPHTHOSTYRILS FROM 1,8-NAPHTHALENE COMPOUNDS

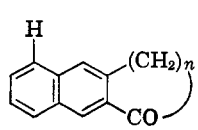


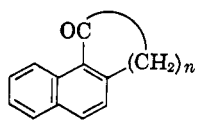
Starting compound (1,8-naphthalenes)	Conditions	Product (naphthostyril)	Yield, %	Ref
8-Amino-1-carboxy	Aq NaOAc, 75°, 40 min	Unsubstituted	...	244
	Fuming HCl	5,6-Dichloro	Good	180
8-Acetamido-1-carboxy-3,4-dihydro	Aq NaOAc, 75°, 40 min	1-Acetyl-4,5-dihydro	93	244
1,2,3,4-Tetrahydro-1-carboxy-8-amino	Aq NaOAc, 75°, 40 min	2a,3,4,5-Tetrahydro	85	180, 244
1-Carboxy-8-carboxamido	Alkaline soln of NaOCl or NaOBr	Unsubstituted	...	125
1-Carboxy-5-bromo-8-amino	Boil with C_2H_5OH	6-Bromo	...	180
1-Carboxy-3-halo-8-amino	Heat on a steam bath	4-Halo	91–96	315
1-Carboxy-4-halo-8-amino	Heat on a steam bath	5-Halo	91–96	315
1,4-Dicarboxy-8-amino	Lactonization	5-Carboxy	...	240
1-Carboxy-3,8-diamino	Lactonization	4-Amino	...	240
1,2-Dihydro-1-carboxy-3-methoxy-8-amino (as sodium salt)	Heat with acetic anhydride in nitrogen at 90° for 15 min	2a,3-Dihydro-1-acetyl-4-methoxy	...	244
1,2-Dihydro-1-carbethoxy-3-methoxy-8-amino	Heat with acetic anhydride in nitrogen at 90° for 15 min	2a,3-Dihydro-1-acetyl-4-methoxy	...	247
1-Carboxy-8-bromo	NH_3, 130–150° for 1 hr, NH_4NO_3, Cu-bronze, $KClO_3$ in autoclave NH_3,	Unsubstituted	82	501
	130–150°, 1 hr, autoclave	Unsubstituted	67	501
	Open vessel	Unsubstituted	52–67	501
	30% aq NH_3, 150° or in the presence of Cu powder at ordinary pressure	Unsubstituted	...	144
1-Carboxy-8-iodo	30% aq NH_3, 150° or in the presence of Cu powder at ordinary pressure	Unsubstituted	...	144
1-Carboxy-5,8-dibromo	30% aq NH_3 150° or in the presence of Cu powder at ordinary pressure	6-Bromo	...	144
1-Carboxy-3-nitro-8-bromo	30% aq NH_3, 150° or in the presence of Cu powder at ordinary pressure	4-Nitro	...	144
1-Carboxy-4-nitro-8-bromo	30% aq NH_3, 150° or in the presence of Cu powder at ordinary pressure	5-Nitro	...	144
1-Chloroformyl-8-bromo	$PhNHNH_2$; MgO in butanol; catalytic amounts of Cu and $Cu(OAc)_2$, 4–5 hr	N-Anilino	50	168
 X=H or Br	MgO–butanol, Cu–$Cu(OAc)_2$, heat 6 hr		...	168, 169
1,6-Disulfo-8-cyano	$Ca(OH)_2$, 250°	7-Sulfo	...	267, 290

derivatives with sulfur in the *peri* ring are given in Table XXXV. Tables XXXVI–XXXVIII contain data on additional types of *peri*-derivatives.

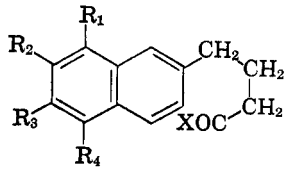
2. *peri* Effects on 1,2 Cyclization

2-Naphthylalkanoic acids (and related compounds) may be expected to undergo cyclization to give the linear annellated compounds (CXXXIV) or the angularly annellated compounds (CXXXV). The presence of *peri*-hydrogen or any other C_8 substituent seems to prevent the formation of CXXXV. In many instances,

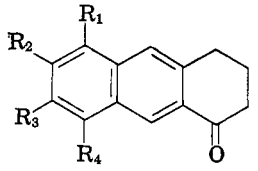

CXXXIV


CXXXV

the ring closure occurs at the 3-position. Thus the cyclization of γ-(8-methyl-2-naphthyl)butyric acid (CXXXVIa) gives 1-keto-1,2,3,4-tetrahydro-5-methylanthracene(CXXXVIIa) and not the ketophenanthrene derivative (262). Similarly, cyclization of CXXXVIb affords only the corresponding ketoanthracene

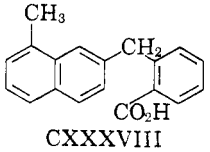


CXXXVIa, X = OH; $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
b, X = OH; $R_1 = R_2 = R_3 = R_4 = CH_3$
c, X = C_2H_5; $R_1 = R_2 = R_3 = R_4 = H$

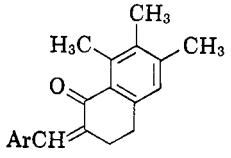


CXXXVIIa, $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_2 = R_3 = R_4 = H$

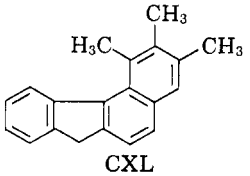
CXXXVIIb (270), and the cyclization of CXXXVIc with PPA affords only 1-ethylanthracene instead of the expected 4-ethylphenanthrene (84). In the latter case, even the steric effect of *peri*-hydrogen seems to be sufficient to direct the ring closure away from the 1-position. Fieser and Hershberg (205) have studied the cyclodehydration of *o*-(8-methyl-2-naphthyl)methylbenzoic acid (CXXXVIII) and obtained a ketonaphthacene derivative but not a benzanthrone. A recent example of this type is the low yield observed in the PPA cyclization of CXXXIX to give CXL or its analogs (122).



CXXXVIII

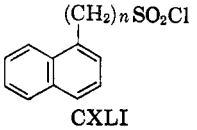


CXXXIX
Ar = C_6H_5 or 1-$C_{10}H_7$

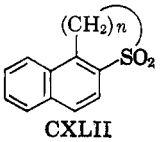


CXL

Cyclization of 1-naphthylalkanesulfonyl chlorides (CXLI) in the presence of aluminum chloride in nitrobenzene solution may be expected to go by *peri* ring

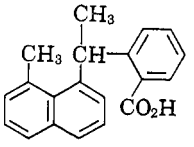


CXLI

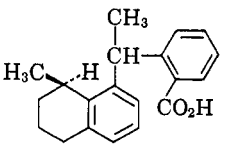


CXLII

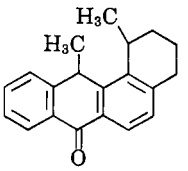
closure, especially with CXLI, $n = 2$. However, the products are only 1,2 ring sulfones CXLII, the yields being 54 ($n = 2$), 65 ($n = 3$), and 16% ($n = 4$) in the cases studied (550). It has not been possible to cyclize acid CXLIII by a variety of procedures, again presumably due to *peri* effects. The carboxyl group in the



CXLIII



CXLIV



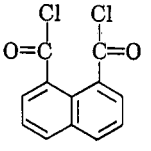
CXLV

benzene ring may be twisted away from the vicinity of the naphthalene ring, thus precluding ring closure (129). However, the partially saturated acid CXLIV is found to undergo smooth cyclization in high yields to CXLV on treatment with hydrogen fluoride or acetic anhydride–acetic acid (130). The *peri* hindrance to cyclization so effective in CXLIII appears to have been overcome in CXLIV.

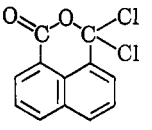
3. *Ring–Chain Tautomerism of ortho- and peri-Disubstituted Structures*

peri-Carbonyl compounds have been found to display several properties which seem to be characteristic of that molecular frame work. When appropriate *peri* substituents are present in the nucleus, by virtue of the proximity, the substituents may give rise to ring–chain tautomerism (360). A number of such cases may be culled from the literature.

Mason (409) observed that the properties and reactions of 1,8-naphthalyl chloride could be satisfactorily



CXLVI

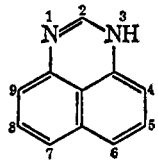


CXLVII

explained only by assuming it to be a mixture of CXLVI and CXLVII. Unlike phthaloyl chloride, it is extremely unstable. The crystals lose their luster even when kept in sealed tubes and decompose readily with water to give naphthalic anhydride. The compound fumes on exposure to air. Davies and Leeper (154) have also suggested a ring structure for this compound. After reviewing the available evidences, French and Kircher (218) believe that both the symmetrical open-chain structure and the ring structure should be in equilibrium.

French and Kircher (219) have also considered the case of 8-benzoyl-1-naphthoic acid and its acid chloride in considerable detail. The *peri* acid exists in two different forms depending upon the solvent used for crystallization (mp 110° from chloroform, ethanol, or 70% acetic acid and 129° from hydrocarbon solvents). The ultraviolet absorption curves indicated a naphthalide structure (CXLIX) rather than a keto structure (CXLVIII). This was also confirmed by a blue fluorescence in ultraviolet light which is charac-

TABLE XXXIII
PERIMIDINES FROM 1,8-NAPHTHALENE COMPOUNDS



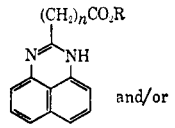
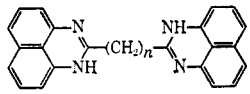
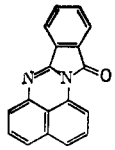
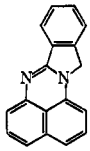
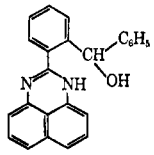
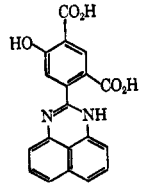
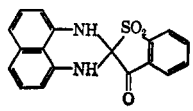
Starting compound	Conditions	Product	Yield, %	Ref
1,8-Naphthalenediamine	90% HCO_2H, heat on water bath	Unsubstituted	80	562
	HCO_2H, heat for 30 min	Unsubstituted	47	592
	HCO_2H	Unsubstituted	...	505
	$HCONPh_2$, 160° for 90–150 min	Unsubstituted	80	562
	CH_3CO_2H, heat for 30 min	2-Methyl	50	592
	$CH_3CH_2CO_2H$, heat	2-Ethyl	90	505
	$CH_3CH_2CH_2CO_2H$, heat	2-*n*-Propyl	Quant	505
	$CH_2(CO_2H)_2$	2-Methyl[a]	...	505
	$CH_2(CO_2C_2H_5)_2$	2-Carbethoxymethyl	...	505
	$(CH_2)_n(CO_2R)_2$ (n = 0 to 8, R = H or Et), heat	 and/or 		488
	$C_6H_5CO_2H$, heat	2-Phenyl	50	592
	$(C_6H_5CO)_2O$, heat in C_6H_6, 2 hr	2-Phenyl	80	586
	Phthalic anhydride, melt		...	505
	Phthalic anhydride, heat	As above	...	561
	Phthalic anhydride, heat in toluene	2-(*o*-Carboxyphenyl)	...	505
	Phthalide, 180–200°, 1 hr		80	88
	Phenylphthalide, 70–100°		...	88
	4-Hydroxy-5-carboxyphthalic anhydride, boil with $C_6H_3Cl_3$, 5 hr		...	191
	3-Nitrophthalic acid, heat in toluene	2-(2-Carboxy-3-nitrophenyl)	...	505
	o-Sulfobenzoic anhydride, heat in $C_6H_3Cl_3$ at 212–215°			192

TABLE XXXIII (*Continued*)

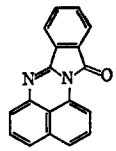
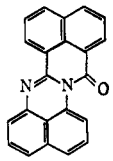
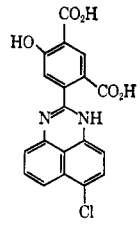
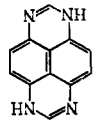
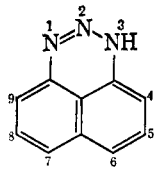
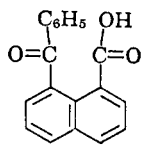
Starting compound	Conditions	Product	Yield, %	Ref
1,8-Napthalenediamine	*o*-Carboxybenzaldehyde		Small	526
	p-$(Me_2N)C_6H_4N{=}C(CN)Ph$, 5–15°, acetic acid	2-Phenyl	84	354
	Naphthalic anhydride		...	190
4-Methyl-1,8-naphthalenediamine	$(CH_3CO)_2O$	2,6-Dimethyl	...	540
4-Chloro-1,8-naphthalenediamine	4-Hydroxy-5-carboxyphthalic anhydride, boil with $C_6H_3Cl_3$, 5 hr		...	191
4-Methyl-5-chloro-1,8-naphthalenediamine	CH_3CO_2H	2,6-Dimethyl-7-chloro	...	540
4-Hydroxy-1,8-naphthalenediamine (as hydrochloride)	85% HCO_2H, 1:6 ratio, heat	6-Hydroxy (as hydrochloride)	95	561
	$(CH_3CO_2)O$, 1:1 ratio, heat on boiling water bath	2-Methyl-6-hydroxy (as hydrochloride)	98	561
2,4-Dibromo-8-nitro-1-acetamidonaphthalene	CH_3CO_2H, $SnCl_2$–HCl	2-Methyl-4,6-dibromo	...	277
1-Phenylamino-4-hydroxy-8-acetamidonaphthalene	CH_3CO_2H	2-Methyl-3-phenyl-6-hydroxy	...	507
1-Nitroso-2-hydroxy-8-acetamidonaphthalene	$SnCl_2$–HCl, room temp, 12 hr	2-Methyl-9-hydroxy	...	320
1,4,5,8-Naphthalenetetramine	HCO_2H		...	163

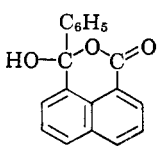
TABLE XXXIV
NAPHTHOTRIAZINES



Starting material	Conditions	Product	Yield, %	Ref
1,8-Naphthalenediamine	HNO_2, CH_3CO_2H, 6°	Unsubstituted	...	6, 465, 563
N-Phenyl-1,8-naphthalenediamine	HNO_2, CH_3CO_2H, 6°	3-Phenyl	...	6, 563
N-Methyl-1,8-naphthalenediamine	HNO_2, CH_3CO_2H	3-Methyl	...	505
N-Phenylsulfonyl-1,8-naphthalenediamine	10% HNO_2, CH_3CO_2H, −10°	3-Phenylsulfonyl	...	428



CXLVIII



CXLIX

teristic of *peri* ring compounds. Esterification by treatment of the silver salt of the acid with ethyl iodide has been shown to give the true ester (from CXLVIII) while conversion of the acid to acid chloride with thionyl chloride followed by ethanolysis gives the pseudo-ester (from CXLIX). These esters can also be differentiated

TABLE XXXV
SULFUR DERIVATIVES FROM *peri* CYCLIZATION

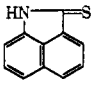
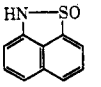
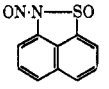
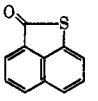
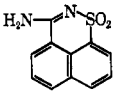
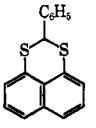
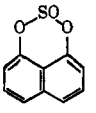
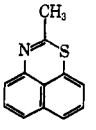
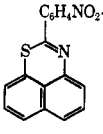
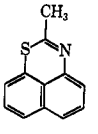
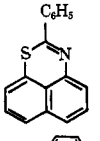
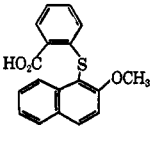
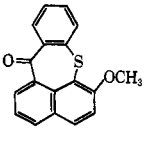
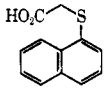
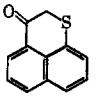
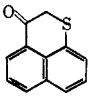
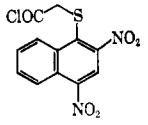
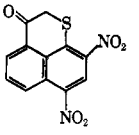
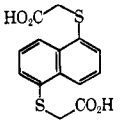
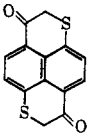
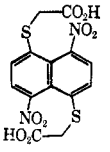
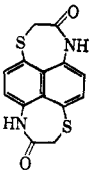
Starting compound	Conditions	Product	Yield, %	Ref
1-Naphthyl isothiocyanate	$AlCl_3$–NaCl		26	167
8-Amino-1-naphthylsulfinic acid	HCl, room temp, 24 hr		...	487
8-Amino-1-naphthylsulfinic acid	Dil NaOH, HNO_2		...[c]	487
8-Bromo-1-naphthoic acid	KSH, $CuSO_4$, Cu, 170°		...	504
8-Cyano-1-naphthylsulfonyl chloride	$SnCl_2$, 80–85°		...	462
8-Cyano-1-naphthylsulfonyl chloride	Satd alc NH_3, heat		...	318
1,8-Dimercaptonaphthalene	Exposure to air or mild oxidizing agent		...	481
	PhCHO		...	481
1,8-Dihydroxynaphthalene	SOCl in CS_2–pyridine		Quant	242
1-Acetamido-8-mercaptonaphthalene (as stannic chloride complex)	$(CH_3CO)_2O$, CH_3CO_2H		93	95, 252
1-(*o*-Nitrobenzamido)-8-mercaptonaphthalene	NaOAc		...	95
1-Acetamido-8-naphthalenethiol acetate	$(CH_3CO)_2O$		57	311
1-Benzamido-8-naphthalenethiol benzoate	Heat with alc NaOH		...	487
	P_2O_5–toluene, heat		35	341

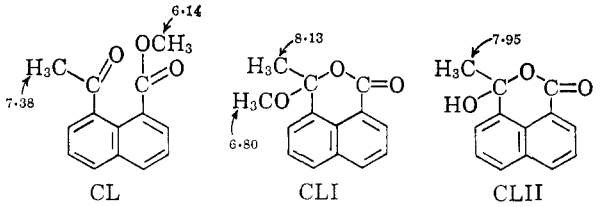
TABLE XXXV (*Continued*)

Starting compound	Conditions	Product	Yield, %	Ref
	$AlCl_3$–C_6H_5Cl, 125°, 5 min		...	460
	$SnCl_4$–C_6H_5Cl, 80°, 10 min		...[a]	459
	$AlCl_3$–CS_2		90	364
	PCl_5, $AlCl_3$–CS_2		Small[b]	365
	$SnCl_2$, HCl, several hours		...	365

[a] 1,2-Cyclization product is also formed. [b] A considerable amount of 1,2 cyclization takes place. [c] This has been refuted recently. The product is shown to be the isomeric sulfone rather than the nitroso sultam (278a).

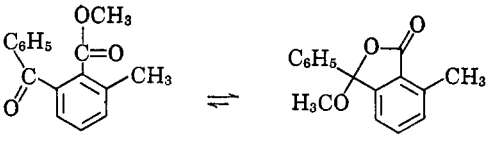
by their fluorescence behavior (219). The acid chloride from CXLVIII has been reported to occur in two forms, an oily form and a crystalline form. The latter is believed to be cyclic as it affords α,α-diphenyl-1,8-naphthalide by Friedel–Crafts reaction with benzene. The oily form reacts vigorously with ethanol (219).

Jones and Lavigne (305) have found that 8-acetyl-1-naphthoic acid lacks the usual reactions of carbonyl compounds, failing to yield the oxime, phenylhydrazone, or semicarbazone. This is also revealed by examining its infrared and nmr spectra (305, 358). The chemical shifts for the different methyl protons in the tautomeric forms of the methyl ester (CL,CLI) provide a clear distinction between these structures. The methyl signal in CLII seems to point to a rapidly estab-

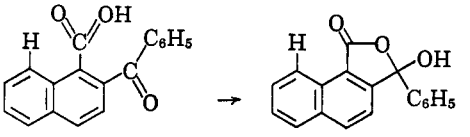


CL CLI CLII

lished acid–pseudo-acid equilibrium in which the pseudo-acid structure is predominant (358). Similar results have been obtained with 8-benzoyl-1-naphthoic acid also and may be general for all 8-aroyl- (or acyl-) 1-naphthoic acids (361). In this connection, it is of interest to mention that the ratio of the normal to pseudo-ester CLIII:CLIV is found to be 40:60 in the case of 2-methyl-6-benzoylbenzoic acid ester (454). In the formally related 2-benzoyl-1-naphthoic acid, the equilibrium



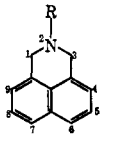
CLIII (40%) CLIV (60%)



CLV CLVI

CLV ⇌ CLVI is entirely in favor of the pseudo-acid (203). The driving force for this shift in the equilibrium in the latter case may arise from two factors: (a) the conjugative interaction of the lactone carbonyl group with the naphthalene ring in CLVI being more than with the phenyl ring in CLIV and (b) the steric assistance by the buttressing effect of the *peri*-hydrogen which could presumably facilitate the ring formation. Without more supporting data, it is difficult to assess the precise role of the *peri*-hydrogen effect. For example, in the preceding case there is some question as to the appropriateness of the comparison between an ester on one hand and an acid on the other. It appears, however, that the data would suggest a greater steric effect from *peri*-hydrogen than from *o*-methyl.

TABLE XXXVI
peri CYCLIZATIONS TO 2,3-DIHYDRO-1H-BENZ[*de*]ISOQUINOLINES



A

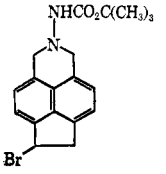
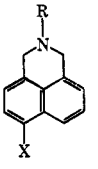
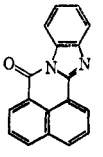
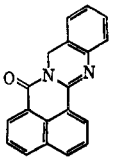
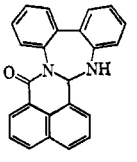
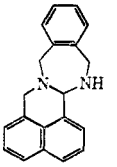
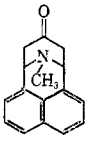
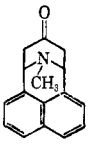
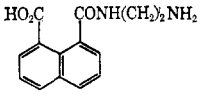
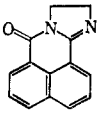
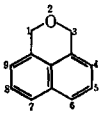
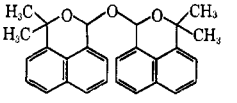
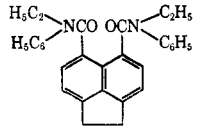
Starting compound	Conditions	Product (A)	Yield, %	Ref
1,8-Bis(bromomethyl)naphthalene	*n*-$BuNH_2$–C_6H_6	R = butyl	...	489
	$C_6H_5CH_2NH_2$–C_6H_6	R = benzyl	88	489
	Cyclohexylamine	R = cyclohexyl	...	489
	$NH_2NHCO_2C(CH_3)_3$–DMF, $N(C_2H_5)_3$, 50–60°, several hours	R = $NHCO_2C(CH_3)_3$	38	127
	$NH_2N(CO_2Bu\text{-}t)_2$	R = $N(CO_2Bu\text{-}t)_2$		126b
5,6-Bis(bromomethyl)acenaphthene	$NH_2NHCO_2C(CH_3)_3$–DMF, $N(C_2H_5)_3$, 50–60°, 30 min, room temp overnight	R = $NHCO_2Bu\text{-}t$	72	128
1-Bromo-5,6-bis(bromomethyl)acenaphthene	$NH_2NHCO_2C(CH_3)_3$–DMF, $N(C_2H_5)_3$, 50–60°, 1 hr		52	128
5,6-Bis(chloromethyl)acenaphthene	$NH_2NHCO_2C(CH_3)_3$–DMF, $N(C_2H_5)_3$, 50–60°, 1 hr	As above, H instead of Br	65	128
4-Substituted (X)-1,8-naphthalic acid (X = SO_3Na, OH, or SH)	RNH_2 (R = CH_3, C_4H_9, C_6H_{11}, CH_2CH_2OH, $C_6H_5CH_2$, C_6H_5, *p*-$N(CH_3)_2C_6H_4$–)			316
8-Carboxy-1-naphthamide	Heat	As above, X = R = H	...	125
8-Carboxy-1-naphthaldehyde	*o*-Phenylenediamine, CH_3CO_2H, heat 7 hr		Small yield	526
	o-Aminobenzylamine, CH_3CO_2H, heat 7 hr		Small yield	527
	o,*o*′-Diaminobiphenyl, CH_3CO_2H, heat 5.5 hr		84	526
	o-$C_6H_4(CH_2NH_2)_2$ as hydrochloride hemihydrate, CH_3CO_2H, NaOAc, heat 6 hr		35	526
	$CO(CH_2CO_2H)_2$, 33% aq CH_3NH_2, $CaCO_3$, boil after 24 hr		...[a]	91

TABLE XXXVI (*Continued*)

Starting compound	Conditions	Product (A)	Yield, %	Ref
	$CO(CH_2CO_2H)_2$, 50% alc CH_3NH_2, pH 6.5, 22°, 5 days		...[b]	91
	230–240°, 15 min		...	89

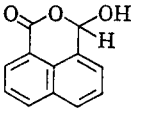
[a] Some amount of A, R = Me is also formed. [b] Exclusive product.

TABLE XXXVII
1H,3H-NAPHTHO[1,8-*cd*]PYRAN DERIVATIVES

Starting compound	Conditions	Product	Yield, %	Ref
1,8-Bis(hydroxymethyl)naphthalene	PBr_3		23	63
	$KHSO_4$, 120°, 10 min	As above	81	573
1,8-Bis(α-hydroxyethyl)naphthalene	Concd HBr, heat	1,3-Dimethyl	...	529
1,8-Bis(α,α′-dihydroxybenzyl)naphthalene	HCO_2H, *p*-$CH_3C_6H_4SO_3H$, heat	1,3-Diphenyl	92	374
	PBr_3	1,3-Diphenyl	85	374
1,8-Bis(α-hydroxy-α,α-diphenylmethyl)-naphthalene	CH_3CO_2H, reflux, 20 hr	1,1,3,3-Tetraphenyl	87	378
	HCO_2H, heat 5.5 hr or dissolve in H_2SO_4	1,1,3,3-Tetraphenyl	91	378
8-Benzhydryl-1-naphthoyl chloride	$SnCl_4$–CS_2, 1.5 hr	1-Hydroxy-1,3-diphenyl	...	359
Free acid of the above	H_2SO_4, steam bath, 2 hr	1-Hydroxy-1,3-diphenyl	...	359
	I_2–CH_3CO_2H or CrO_3–CH_3CO_2H	1-Keto-3,3-diphenyl	7–22	146a
Methyl naphthalate	Excess of C_6H_5Li	1,1,3-Triphenyl-3-hydroxy	...	589
1,8-Dibenzoylnaphthalene	Excess of C_6H_5Li	1,1,3-Triphenyl-3-hydroxy	...	589
8-Isopropyl-1-naphthoic acid	Liquid HF		67	359
	H_2SO_4	As above	55	359
	$SnCl_4$	As above	10–17	359
8-Chloromethyl-1-naphthonitrile	30% aq NaOH, 1.5 hr	3-Keto	25	456
8-Carboxy-1-naphthyl benzyl ketone	P + HI	1-Benzyl-3-keto	60	574
8-Carboxy-1-naphthyl *o*-tolyl ketone	P + HI	1-*o*-Tolyl-3-keto	...	574
8-Carboxy-1-naphthyl 1-naphthyl ketone	P + HI	1-(1-Naphthyl)-3-keto	60–65	574
	60% aq H_2SO_4, reflux, 30 min	1,3-Diketo-6,7-dimethylene	35–40	128

Cyclodehydration of *o*-benzoylbenzoic acid is known to give anthraquinone. A similar reaction does not seem to occur with 8-benzoyl-1-naphthoic acid (410) even though in other cases formation of a seven-membered ketone causes no difficulty (*e.g.*, Table XXX). Presumably the cyclic pseudo-acid structure of this acid is not conducive to such a reaction. A pseudo-acid structure has also been postulated (445) for the ethyl ester of 4-hydroxymethyl-5-phenanthrenecarboxylic acid isolated by Fieser and Novello (206).

A few more examples of ring–chain tautomerism are available among *peri*-formyl- and *peri*-hydroxyketo-



CLVII

naphthalenes. Thus Rodionov and Fedorova (496) have examined the reactions of 8-formyl-1-naphthoic

TABLE XXXVIII
MISCELLANEOUS *peri* CYCLIZATIONS

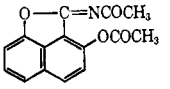
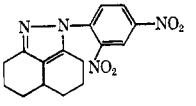
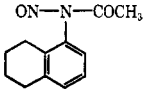
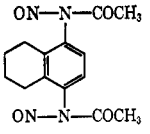
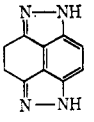
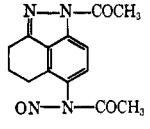
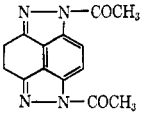
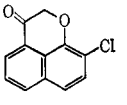
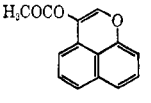
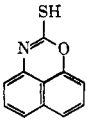
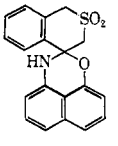
Starting compound	Conditions	Product	Yield, %	Ref
1,8-Dihydroxynaphthalene	Dehydration under nonoxidizing conditions		...	33
8-Bromo-1-naphthoic acid	Boil with aq NaOH, Cu–bronze		47	500
8-Amino-1-naphthoic acid	HNO_2, then heat with dil H_2SO_4	As above	Good	180
2,8-Dihydroxy-1-naphthaldoxime	Fused NaOAc, $(CH_3CO)_2O$, heat 5 hr		75	3
Decalin-1,8-dione	NH_2OH–C_2H_5OH, HCl, heat		84	528
	$N_2H_4 \cdot H_2O$, NaOH		85	528
	2,4-Dinitrophenylhydrazine–CH_3OH		...[b]	319
	Heat in C_6H_6		40	557
	Heat in C_6H_6		...	557
	Heat in C_6H_6		...	557
β-(8-Hydroxy-1-naphthyl)ethanol	PBr_3, reflux, 15 min		75	456
2-Chloro-1-naphthoxyacetyl chloride	$AlCl_3$–C_6H_6, 4.5 hr		50[c]	456
8-Carboxy-1-naphthoxyacetic acid	Boil with $(CH_3CO_2)O$, 30 min		50[d]	456
8-Amino-1-naphthol	CS_2, KOH–C_2H_5OH, reflux		...	421
8-Amino-1-naphthol	*o*-Sulfobenzoic anhydride, $C_6H_6Cl_2$, 210–215°		90	192

TABLE XXXVIII (*Continued*)

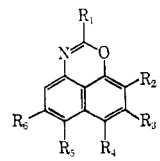
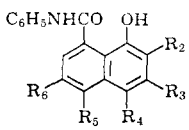
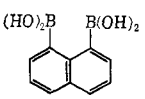
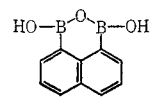
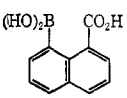
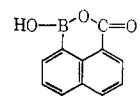
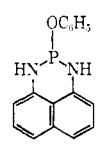
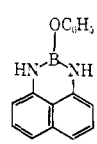
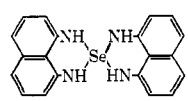
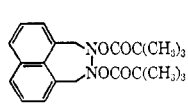
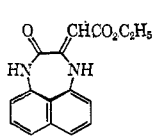
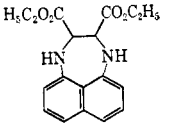
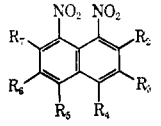
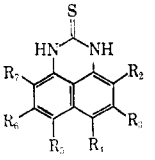
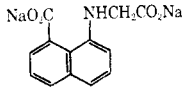
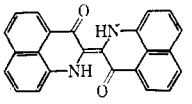
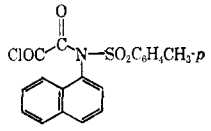
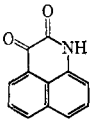
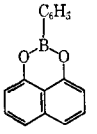
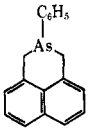
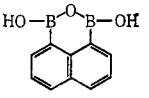
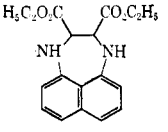
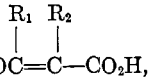
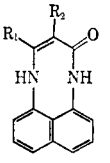
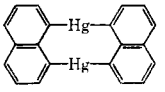
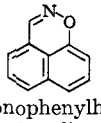
Starting compound	Conditions	Product	Yield, %	Ref
8-Acetamido-1-naphthol	Distil	 $R_1 = CH_3$, $R_2 = R_3 = R_4 = R_5 = R_6 = H$	...	94
8-Acetamido-1-naphthol	Br_2–CH_3CO_2H	As above, $R_1 = CH_3$, $R_2 = R_4 = R_5 = Br$, $R_3 = R_6 = H$ (as the dibromide)	...	197
	Cl_2 (gas) in CH_3COCH_3	As above, $R_1 = CH_3$, $R_2 = R_4 = R_5 = Cl$, $R_3 = R_6 = H$	...	198
8-Benzamido-1-naphthol	Br_2–CH_3CO_2H, heat	As above, $R_1 = C_6H_5$, $R_2 = R_4 = R_5 = Br$, $R_3 = R_6 = H$	...	197
 $R_2 = R_3 = R_4 = R_5 = R_6 = H$				
$R_2 = NH_2$, $R_3 = R_5 = SO_3Na$, $R_4 = R_6 = H$		As above, $R_1 = C_6H_5$, $R_2 = NH_2$, $R_3 = R_5 = SO_3Na$, $R_4 = R_6 = H$	...	434
$R_2 = NH_2$, $R_3 = R_6 = SO_3Na$, $R_4 = R_5 = H$		As above, $R_2 = NH_2$, $R_1 = C_6H_5$, $R_3 = R_6 = SO_3Na$, $R_4 = R_5 = H$	...	434
$R_2 = NH_2$, $R_3 = R_4 = R_6 = H$, $R_5 = SO_3Na$		As above, $R_2 = NH_2$, $R_1 = C_6H_5$, $R_3 = R_4 = R_6 = H$, $R_5 = SO_3Na$	...	434
	Melt			380
	P_2O_5, 56° (2 mm), several hours		...	380
1,8-Naphthalenediamine	$(C_6H_5O)_3P$, 180° (10 mm), 6 hr		13	477
	$(C_6H_5O)_3B$, 110° (10 mm), 10 min		...	477
	H_2SeO_3, heat, 6 hr		...	272
1,8-Bis(bromomethyl)naphthalene	[KNCOCOC$(CH_3)_3$]–DMF, room temp, 20 hr		42	126a
1,8-Naphthalenediamine	$C_2H_5OCOC{\equiv}CCOOC_2H_5$, C_2H_5OH	 and	13	296

TABLE XXXVIII (*Continued*)

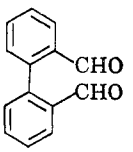
Starting compound	Conditions	Product	Yield, %	Ref
			41	296
 (a) $R_2 = R_5 = CH_3$ (b) $R_2 = R_3 = CH_3$ (c) $R_2 = R_6 = CH_3$	Reduction, then CS_2		...	324
	NaOH, $NaNH_2$, 260–300°		...	177
			...	509
1,8-Dihydroxynaphthalene	CH_2SO_4		...	124
	Phenylboric acid		83	470
1,8-Bis(bromomethyl)naphthalene	$C_6H_5AsH_2$–C_6H_6, 0°		60	63
1,8-Dilithionaphthalene	$(C_4H_9O)_3B$–H_2O, heat		...	380
1,8-Naphthalenediamine	$CHBrCO_2C_2H_5$ | $CHBrCO_2C_2H_5$, pyridine, heat, 2 hr		6	296
	 180° in inert solvent or 120° without solvent (a) $R_1 = C_6H_5$, $R_2 = H$ (b) $R_1 = C_6H_5$, $R_2 = CH_2C_6H_5$ (c) R_1 = 3-pyridyl, $R_2 = H$		...	296
1,8-Bis(chloromercury)naphthalene	NaI–C_2H_5OH, reflux, 50 hr		94	380

[a] Refluxing with acetic anhydride for 1 hr gives 

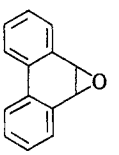
[b] This is contrary to the reported isolation of a monophenylhydrazone in this reaction by Stetter and Milbers (528). [c] In the absence of a 2-chloro substituent, 1,2 cyclization and not *peri* cyclization occurs; see ref 456. [d] Obviously formed through the enol.

acid and found that its reactivity could be explained by invoking a ring structure CLVII (p 611).

Aromatic dialdehydes on treatment with bis(dimethylaminophenyl)phosphine give rise to epoxides, and the reaction is suggested to proceed through formation of ylides as intermediates (400, 453). For example, 9,10-dihydrophenanthrene 9,10-epoxide (CLIX) is obtained from *o,o'*-diformylbiphenyl (CLVIII). The nonoccurrence of this reaction with 1,8-diformyl-

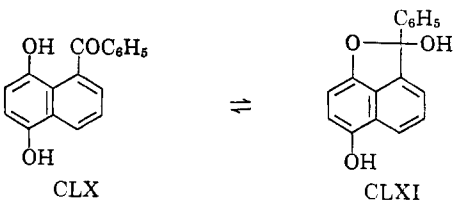


CLVIII



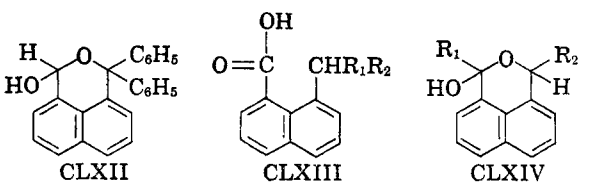
CLIX

naphthalene might be ascribed to mutual steric interference of the aldehyde groups, preventing reaction with the diarylphosphine. Newman and Blum (453) do suggest that *peri*-diformylnaphthalene may exist as a cyclic species but refrain from postulating any specific structure for this. Another instance of ring–chain tautomerism is provided by 5,8-dihydroxy-1-naphthyl phenyl ketone (CLX, CLXI) (511).



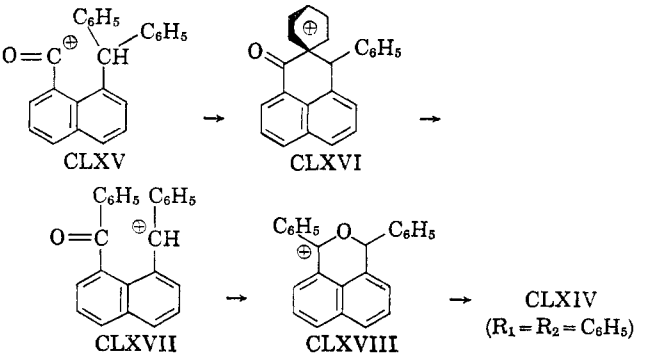
CLX ⇌ CLXI

Rather unusual types of rearrangements involving *peri*-naphthoic acids and their derivatives have been exhaustively investigated in Letsinger's laboratories (359, 373–377). When the hemiacetal CLXII is heated for 30 min with formic acid or with acetic acid con-



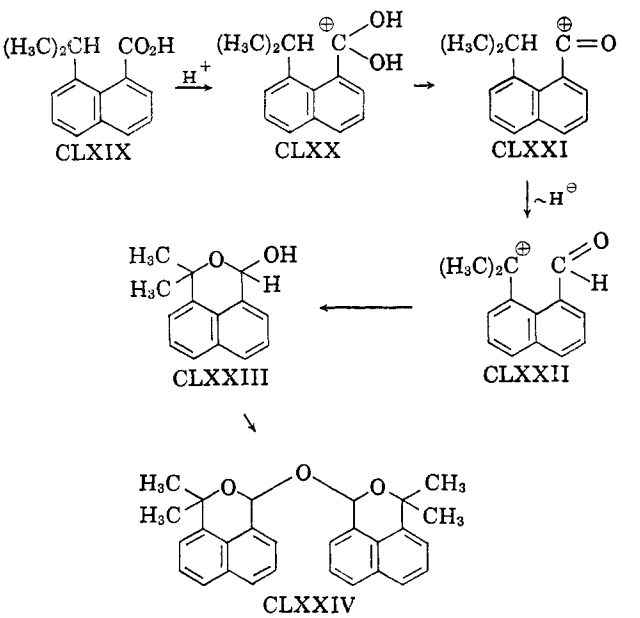
CLXII CLXIII CLXIV

taining iodine or sulfuric acid, it is quantitatively isomerized to 8-benzhydryl-1-naphthoic acid, and the isomerization is reported to proceed by 1,5 hydride shift (374). A more interesting reaction involves the migration of phenyl group across the *peri* positions (359, 373). Thus, 8-benzhydryl-1-naphthoic acid chloride (from CLXIII, $R_1 = R_2 =$ Ph) on treatment with stannic chloride in carbon disulfide is converted to CLXIV in 90% yield. The rearrangement is said to proceed by the following scheme.



CLXV CLXVI CLXVII CLXVIII CLXIV ($R_1 = R_2 = C_6H_5$)

Carefully designed experiments have ruled out the possibility of intermolecular mechanism for the reaction (359). Encouraged by these results, 8-isopropyl-1-naphthoic acid was also subjected to conditions which caused rearrangement in 8-benzhydryl-1-naphthoic acid. There is no indication of an analogous 1,5 methyl shift. Indeed the migration of methyl groups beyond the common 1,2 shift is reportedly rare (375). In the isopropyl acid case, the reaction appears to occur in the following fashion.

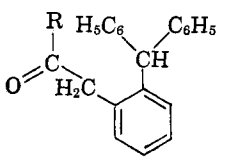


CLXIX CLXX CLXXI CLXXII CLXXIII CLXXIV

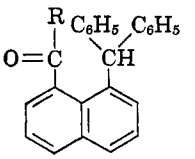
A novel feature of the proposed mechanism is a hydride transfer from an alkyl group to an acylium ion which is not common. The occurrence of such a facile transfer is presumably a manifestation of a proximity effect (375).

The reaction of 5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid with concentrated sulfuric acid or liquid hydrogen fluoride leads to a product similar to CLXXIV obtained from 8-isopropyl-1-naphthoic acid, involving probably a similar reaction path. The fact that the presence of *peri*-isopropyl group is critical for the rearrangement is borne out by the absence of such a reaction with 5,6,7,8-tetrahydro-1-naphthoic acid (lacks the 8-isopropyl group) or *o*-isobutylbenzoic acid (lacks the

peri disposition of the groups) under comparable conditions (376). Similarly, only negative results are witnessed in the attempted rearrangement of 2-benzhydrylphenylacetic acid (CLXXV, R = OH) or the acid chloride (CLXXV, R = Cl) despite its formal structural resemblance to 8-benzhydryl-1-naphthoic acid (CLXXVI, R = OH) (377).

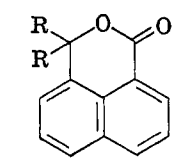


CLXXV

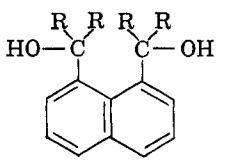


CLXXVI

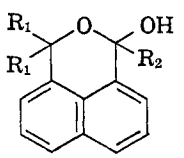
The extreme ease with which the above rearrangements proceed involving a smooth *peri* ring closure would suggest that the presence of the *peri* ring in the product confers considerable stability to the resulting system. Indeed several workers have testified to this fact before. Lactones derived from *peri*-naphthalene derivatives are found to be remarkably stable. Geissman and Morris (234) have observed that the reaction of diphenyl-1,8-naphthalide(CLXXVIIb) with alkylmagnesium halides (alkyl being ethyl, isopropyl, *n*-butyl, and *sec*-butyl) gives only hemiketals CLXXIX and not the glycols. The failure of the reaction to proceed beyond the mono-addition stage is presumably due to the stability of the *peri* ring since glycol formation would of necessity involve ring scission at some stage. Earlier also, Wittig, Leo, and Weimer (589) have noticed that addition of phenylmagnesium bromide to diphenylnaphthalide (CLXXVIIb) stopped at the hemiacetal stage (CLXXIX) and no 1,8-bis(α-hydroxybenzhydryl)naphthalene(CLXXVIIIb) could be isolated. The stability of the *peri* ring in CLXXVIIb is attributed to the spatial features of the ring



CLXXVIIa, R = CH_3
b, R = C_6H_5



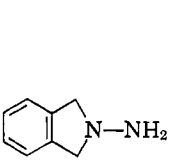
CLXXVIIIa, R = CH_3
b, R = C_6H_5



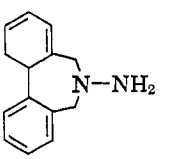
CLXXIXa, $R_1 = R_2 = C_6H_5$
b, $R_1 = C_6H_5$
R_2 = alkyl

and the stabilizing effect of the *gem*-phenyl group. CLXXVIIb does not undergo hydrolysis even on boiling with 20% potassium hydroxide. The stability of dimethyl-1,8-naphthalide (CLXXVIIa) is even more remarkable. It is not cleaved by heating at 150° for 40 hr with 25% aqueous alkali or by heating at 100° with concentrated ammonia for 45 hr. Furthermore, it could not be reduced with such vigorous reducing agents as aqueous hydriodic acid and red phosphorus (reflux, 65 hr) or zinc amalgam in the presence of hydrochloric acid–formic acid (at reflux, 30 hr) (375). In contrast, the parent naphthalide (CLXXVII, R = H) is readily reduced under Clemmensen conditions (224a). The saponification of CLXXVIIa could, however, be effected by heating at 145° with potassium hydroxide in triethylene glycol for several hours (375).

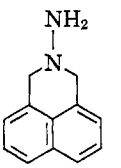
The experiments of Carpino (126a, 128) on the alkaline decomposition of the N-*p*-toluenesulfonyl derivatives of CLXXX, CLXXXI, and CLXXXII also indicate the stability of the *peri* ring compound. While the



CLXXX



CLXXXI



CLXXXII

tosyl derivatives of CLXXX and CLXXXI are readily attacked by aqueous alkali, CLXXXII is found to be unaffected under these conditions. This perhaps is partly due to the optimum ring size also.

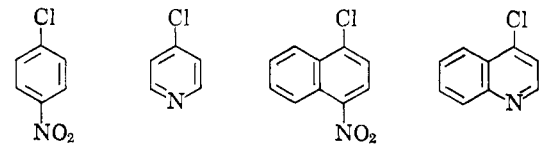
B. *peri* EFFECTS ON CHEMICAL REACTIVITY OF SUBSTITUTED NAPHTHALENE DERIVATIVES

1. *Studies Involving Quantitative and Semiquantitative Measurements*

Steric strain in the transition state of a substrate during a chemical reaction is known to influence the rate and sometimes even the course of the reaction. It has also been established that such strain may cause either a rate acceleration or deceleration depending upon the mechanistic details of the reaction. Among naphthalene derivatives the reactivity of a functional group at the 1-position is often different from that at the 2-position. While part of this difference is undoubtedly due to the differing electronic interaction of the substituent with the nucleus at these positions, the steric effect of the *peri* substituent also appears to be a significant factor. This section is a survey of the results obtained from quantitative studies undertaken to examine this aspect of naphthalene chemistry. A wide variety of reactions have been followed kinetically for this purpose including (a) the nucleophilic displacement (SN2) of halogen from activated or nonactivated naphthyl halides, (b) saponification of esters from aroic and arylacetic acids, and (c) solvolysis of arylcarbinyl halides. The data are so widely scattered in the literature that a complete account of them is difficult to achieve.

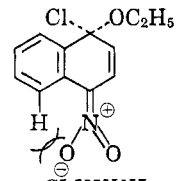
Illuminati and Tarli (294) have compared the reactivities of a series of aza- and nitro-activated aromatic

chlorides with sodium methoxide. The increased rate in the naphthalene as compared to the benzene series



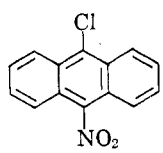
CLXXXIII	CLXXXIV	CLXXXV	CLXXXVI
10^5 k at 60° l. mole^{-1} sec^{-1}			
7.24	0.479	38.3	4.57

presumably reflects the inductive effect of the second aromatic ring augmented, possibly by a relief of steric strain (*peri* interaction) at the reaction site in the transition state (see CLXXXVII). The fact that the increase in rate for the aza compound ($k_{CLXXXVI}/k_{CLXXXIV}$ = 9.6) is greater than for the nitro compound ($k_{CLXXXV}/k_{CLXXXIII}$ = 5.3) probably reflects increased importance of steric inhibition of resonance in the latter, since the nitro group can exercise its full activating effect toward nucleophilic substitution only when it is coplanar with the ring in the transition state; this situation is sterically inhibited in the case of CLXXXV (see CLXXXVII).

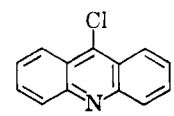


CLXXVII

The effect is seen to a much more marked degree in the anthracene analogs CLXXXVIII and CLXXXIX (478); thus $k_{CLXXXVIII}/k_{CLXXXIX}$ (0.056) is markedly less than $k_{CLXXXV}/k_{CLXXXVI}$ (8.0) which, as mentioned above, is already smaller than $k_{CLXXXIII}/k_{CLXXXIV}$ (15.1).



CLXXXVIII



CLXXXIX

Piperidino dehalogenation of naphthyl halides has been studied by several authors to investigate the stereoelectronic effects in naphthalene (80, 85, 99, 417, 506, 553, 554). McLeish and Campbell (417) have observed that the percentage removal of the halide ion (in 30 min) is slightly less for 1-nitro-2-halonaphthalenes compared to 2-nitro-1-halo isomers. The reactivity of 4-nitro-1-halonaphthalenes roughly equals that of the obviously hindered 1-nitro-2-halonaphthalenes. Further, no reaction seems to occur with 5-nitro-1,4-dibromonaphthalene, even after 20 hr. In all these instances, *peri* interaction (causing steric inhibition of resonance of the nitro substituent) is presumably the decelerating force. Conflicting data have been obtained with respect to 8-nitro-1-halonaphthalene in which the nitro group is located in a nonactivating (*meta*-like) as well as *peri* position. Complete lack of reactivity is reported (417) for 8-nitro-1-chloronaphthalene on treatment with piperidine at 45° over 20 hr whereas a high conversion of 92% is indicated in the reaction of the bromo isomer with the same reagent at 125° in presence of copper sulfate. Presumably the mechanism of the reaction itself is different under these conditions.

Berliner, Quinn, and Edgerton (80) have studied the piperidine displacement reaction in detail with a number of halo compounds and their results are given in Table XXXIX. Of the nonactivated halides, the 1 isomers

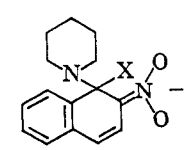
TABLE XXXIX

REACTION OF HALONAPHTHALENES WITH PIPERIDINE[a] (80)

Naphthalene	10^4k/hr
1-Chloro	1.48
2-Chloro	1.86
1-Bromo	8.56
2-Bromo	14.9
1-Iodo	17.0
2-Iodo	21.1
1-Chloro-2-nitro	46,000
2-Chloro-1-nitro	4,700
1-Bromo-2-nitro	55,100
2-Bromo-1-nitro	6,130
1-Iodo-2-nitro	8,560
2-Iodo-1-nitro	760

[a] Data for the simple halides are at 165° and for the nitrohalides at 25°. Rate values are also furnished at 200° for the simple halides and at 0° for the activated ones. The trends are found to be similar.

react slower than the 2 isomers, consistent with a simple SN2 process. (Each halide gives the corresponding piperidine compound, so a benzyne intermediate is not involved.) Among the activated halides the dramatic difference between 1-nitro-2-halo- and 2-nitro-1-halo isomers is attributed to steric inhibition of resonance in the transition state in the former case, considerably diminishing the activating influence of the 1-nitro group. The displacement of the halogen in the nonactivated halides is considered to be SN2. With the nitro halides, a two-step process is envisioned: (i) formation of a fairly stable intermediate CXC and (ii) the cleavage of the carbon–halogen bond. The displacement rates seem to indicate that the formation of the intermediate is the rate-determining step since

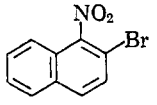


CXC

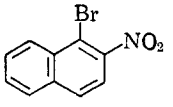
the rate falls off with increasing size of the halogen. If step (ii) is rate controlling, the iodo compound should

show a much higher reactivity since iodide ion is a better leaving group.

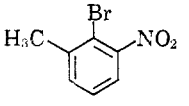
In another study of the reactivity of nitrobromonaphthalenes toward piperidine, 1-bromo-8-nitronaphthalene has been found (85) to react 450 times faster than 1-bromonaphthalene. Its reactivity is nearly equal to that of 3-nitro-1-bromonaphthalene. It is not certain whether the activation of the halogen in the *peri* derivative is due to a field effect or due to relief of steric strain at the reaction site in the transition state. van Berk, Verkade, and Wepster (85) have also considered the relative reactivity of 1,2 and 2,1 nitrobromonaphthalenes and their benzene analogs in this reaction. In agreement with the earlier observation (417), the 1-nitro isomer (CXCI) reacts slower than the 2-nitro compound (CXCII). In the benzene series, CXCIII is strongly deactivated by the presence of *o*-methyl



CXCI



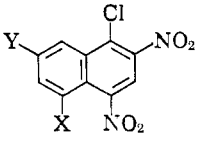
CXCII



CXCIII

and its reactivity is $^1/_{120}$th that of *o*-nitrobromobenzene. However, the sterically related naphthalene derivative CXCII is the most reactive of its class. It would then seem that *peri*-hydrogen hindrance is much less than that due to an *o*-methyl group (85). One has to be cautious in taking such a view because of the uncertain manner in which molecular distortions seem to affect chemical reactivity of overcrowded compounds. For example, 4,5-dinitro-1-bromonaphthalene is found to react much faster than 4-nitro-1-bromonaphthalene in its reaction with sodium ethoxide or piperidine (506). It is difficult to explain this result without invoking a distortion which presumably leads (in some way obscure at the moment) to activation of the halogen by the nitro groups.

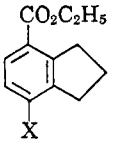
Elias and Parker (182) have compared the rate constants for the reaction of 2,4-dinitrochlorobenzene and picryl chloride with aniline in ethanolic solution with the rates obtained for 1-chloro-2,4-dinitro- and 1-chloro-2,4,5-trinitronaphthalenes. In the former pair, the addition of a third nitro group causes a 16,100-fold rate increase, while the increment in the naphthalene compounds is a mere 14. The reasons for this vast difference may be (a) a decrease in the inductive effect of the third nitro group in CXCIVb because of the intervening distance between the reaction site and the nitro group,



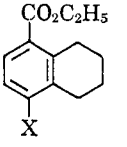
CXCIVa, X = Y = H
b, X = NO_2, Y = H
c, X = H, Y = NO_2

(b) a decrease in the electromeric effect of the substituent because it is not in the same ring as the reaction site, and (c) a mutual reduction of the activating effect of the *peri*-nitro groups due to steric compression. As suggested by these workers, a determination of the relative reactivity of the unhindered 1-chloro-2,4,7-trinitronaphthalene (CXCIV c) would indeed be of interest.

We may now digress to review some studies on saponification rates of naphthoic esters that have a bearing on *peri* interaction. The steric effect of the methylene groups has been compared in the hydrindan and tetralin derivatives (CXCV, CXCVI) (194). The observed



CXCVa, X = H
b, X = $N(CH_3)_2$



CXCVIa, X = H
b, X = $N(CH_3)_2$

hydrolysis rate constants (10^3k in l. mole^{-1} sec^{-1} at 25°) for these derivatives are CXCVa, 8.55; CXCVb, 1.68; CXCVIa, 2.69; CXCVIb, 1.16. In CXCVb and CXCVIb the presence of the dimethylamino group should result in a decrease in the hydrolysis rates relative to CXCVa and CXCVIa, respectively, because of its strong mesomeric effect. However, this effect can come into full play only when the carboalkoxy and amino groups are planar with the aromatic ring. This is sterically opposed by the *peri*-methylene hydrogens of the five- or six-membered ring (194). The ratio k_{CXCV_a}/k_{CXCV_b} (5.10) is greater than k_{CXCVI_a}/k_{CXCV_b} (2.32), indicating the larger steric effect of the methylene group in the six-membered ring. It might also be noted that $k_{CXCVI_a} < k_{CXCV_a}$ is in itself a manifestation of the greater *peri* interaction of the methylene group on the six-membered (as compared to five-membered) ring in the transition state for saponification.

That the mesomeric effect of a dimethylamino group is considerably weakened by *peri*-hydrogen is substantiated by studies in the naphthoate series also (212, 482). Price and Michel (482) have reported the rates of alkaline hydrolysis for a group of ethyl 2-naphthoates in 70% dioxane at 25° (Table XL). The rate decrease in the 8-amino compound compared to the unsubstituted

TABLE XL
RATES OF ALKALINE HYDROLYSIS OF ETHYL 2-NAPHTHOATES[a] (482)

Compound	10^3k, l. mole^{-1} sec^{-1}
Ethyl 2-naphthoate	3.46
Ethyl 5-amino-2-naphthoate	2.50
Ethyl 8-amino-2-naphthoate	1.20
Ethyl 8-dimethylamino-2-naphthoate	2.46
Ethyl 5-nitro-2-naphthoate	31.4
Ethyl 8-nitro-2-naphthoate	20.0

[a] In 70% dioxane, 25°.

ester is understandable since the amino group increases electron density at the 2-position by mesomeric interaction. By the same token, the rate should be even less for 8-dimethylamino ester. The unexpected increase is therefore considered to arise from loss of mesomeric interaction of the 8-substituent. The fact that the rate is not larger than that of the simple ester suggests that the dimethylamino group is not twisted sufficiently to make it orthogonal to the ring. If it were, then acting inductively, it should have caused a rate enhancement. The data on the nitro esters also indicate a similar dampening of nitro group resonance with the ring in ethyl 8-nitro-2-naphthoate. Otherwise the effect of the 8-nitro group should, of course, be relayed (by resonance) to the β-carbon atom on the ring more effectively than that of a 5-nitro group (which acts by an inductive effect only) (482).

Additional papers (211, 212, 214, 469) have been published on the kinetics of hydrolysis of substituted 1- as well as 2-naphthoates. Both ethyl and methyl esters of 1-naphthoic acid are found to undergo hydrolysis slower than their 2 isomers. The corresponding amides also exhibit a similar behavior. In the case of ethyl 4-substituted 1-naphthoates, the Hammett σ values for the 4-substituents have been estimated. The deviations between the expected and the observed values are found to be considerable for 4-fluoro, 4-nitro, and especially 4-dimethylamino groups (212). No such deviation has been noticed for 4-methoxyl and it would appear plausible that this group may remain planar but still escape *peri*-hydrogen interaction by adopting a preferred orientation that keeps the methoxyl away.

The rate data for the base-catalyzed hydrolysis of nitro-1-naphthoates are given in Table XLI. The low reaction rates observed for 2-nitro and 8-nitro esters are evidently a consequence of steric effects.

TABLE XLI

HYDROLYSIS OF ETHYL 1-NAPHTHOATES[a] (211, 212)

Substituent	10^3k, l. mole^{-1} sec^{-1}
H	2.50
2-Nitro	0.332
3-Nitro	92.3
4-Nitro	101.0
5-Nitro	34.5
6-Nitro	29.9
8-Nitro	0.0256
4, 5-Dinitro	158.0 (at 20°)

[a] In 85% ethanol, 50°.

In the case of the 2-nitronaphthoate, $\Delta\Delta G$ (the difference in activation energy between the substituted and unsubstituted ester) is large and positive (1.3 kcal/mole), whereas for ethyl *o*-nitrobenzoate it is large but negative (−1.2 kcal/mole). In ethyl *o*-nitrobenzoate, steric interactions are likely to be relieved by bond angle deformations. In the naphthoate case, the ester group cannot bend away from the nitro without seriously interfering with *peri*-hydrogen. Perhaps a better comparison would be with ethyl 6-methyl-2-nitrobenzoate. Yet another point of interest from the data in Table XLI is the extremely high reactivity of the *peri*-dinitro ester. This behavior closely parallels the observations made with *peri*-dinitro compounds in piperidino debromination (85) mentioned earlier or in catalytic deacylations (355) to be discussed later in this section. A possible explanation for the marked rate increase in these cases may lie in a partial loss of aromatic character owing to appreciable puckering of the ring system. However, a fuller understanding of this phenomenon requires further study.

Another series of reactions which has been employed to study *peri* effects in polycyclic systems is the SN1 solvolysis of arylcarbinyl halides (81, 159, 160, 199, 455, 458, 513, 556). The rate of solvolysis is governed by the stability of the carbonium ion intermediate as

$$ArCR_1R_2Cl \longrightarrow Ar\overset{+}{C}R_1R_2 + Cl^- \xrightarrow{ROH} ArCR_1R_2OR$$

R = H, alkyl, or acyl; R_1, R_2 = H, alkyl, or aryl

well as steric factors. In the absence of the latter, the stability of the carbonium ion, and hence the reactivity, should be tertiary > secondary > primary. Steric inhibition of resonance of the carbonium ion, due to *peri*-type interactions (*e.g.*, in 1-naphthylmethyl chloride or 9-anthrylmethyl chloride), was believed to lead to diminished carbonium ion stability in 1-naphthalenoid systems (102, 531), although it now appears that the trend may be explained by electron delocalization effects alone (160a). Among the reactions studied are the ethanolysis of triarylmethyl chlorides (445), solvolysis of α-arylmethyl chlorides in moist formic acid (159, 199) and in aqueous acetone (81, 458), acetolysis of naphthylmethyl bromides (513), and the solvolysis of α-arylbenzyl chlorides (556). At least in the case of triarylmethyl halides, steric inhibition of resonance may be responsible for the rate trends observed. An excellent account of many of these examples is available in Streitwieser's book (531). Related findings are those of Chapman and Triggle (134) in regard to solvolysis rates of N,N-dialkyl-β-aryl-β-bromoethylamines [$ArCH(Br)CH_2N(CH_3)_2$]. The amount of bromide ion liberated (in 5 min) is much less when Ar = 1-naphthyl (24.7%) than when Ar = 2-naphthyl (42.3%).

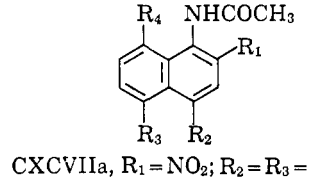
The effect of *peri* interactions on saponification rates has also been studied (2) in the naphthyl acetate series, where the carboxylate group is separated from the ring by a methylene group. The rate constants for the alkaline hydrolysis of methyl aryl acetates in 85% methanol and 75% aqueous acetone obtained with both 1-naphthalene-type and benzene-type compounds are listed in Table XLII. Esters of the former type are seen to possess lower reactivity, clearly indicating that the intervention of a methylene group has not abated *peri*

hindrance. It may be of interest to mention a similar persistence of an *ortho* effect in the saponification of ethyl phenylacetates (570).

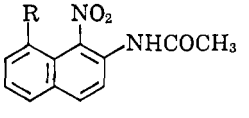
TABLE XLII
SAPONIFICATION RATES OF $ArCH_2CO_2CH_3$ AT 24.9° (2)

Ar	10^3k in 85% methanol	10^3k in 75% acetone
9-Anthryl	0.568	14.4
6-Chrysyl	1.17	41.3
9-Phenanthryl	1.18	40.5
1-Naphthyl	1.19	46.3
1-Pyrenyl	2.01	77.4
p-Tolyl	2.45	110.0
2-Fluorenyl	2.76	...
Phenyl	2.97	136.0
2-Naphthyl	3.64	143.0
4-Biphenylyl	3.66	156.0
2-Anthryl	4.05	166.0
3-Phenanthryl	4.21	168.0
2-Phenanthryl	4.28	169.0

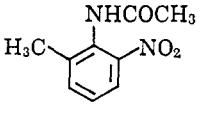
Deacylation of nitroacetnaphthalides (355) involving *peri* substituents by base has also been studied, but the data do not seem to be self-consistent. The rate observed for 1-acetamido-2-nitronaphthalene (CXCVIIa) is about $^1/_{300}$th the rate for the 2,1 isomer (CXCVIIIa). Such a large difference in rates does not seem warranted by electronic factors alone. Steric factors are presumably involved; *peri* interaction causes gross steric hindrance to attack by base in compounds of type CXCVII but affects type CXCVIII only through steric inhibition of resonance (between NO_2 and CH_3CONH). It has been pointed out (355) that the smaller rate observed for the 1-acetamido compound CXCVIIa is due to a far more pronounced steric effect acting on the 1-acetamido



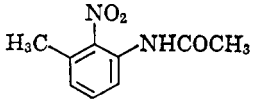
CXCVIIa, $R_1 = NO_2$; $R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = R_3 = H$; $R_4 = NO_2$
c, $R_1 = R_4 = H$; $R_2 = NO_2$; $R_3 = NO_2$ or Br



CXCVIIIa, R = H
b, $R = NO_2$



CIC



CC

group in this compound than on the 1-nitro group in CXCVIIIa. Parallel behavior is found in the benzene analogs CIC and CC, the former being less reactive. However, the extreme reactivity of CXCVIII is not reconcilable with the observed deactivation in CIC which is deacylated $^1/_{80}$th as fast *o*-nitroacetanilide.

A few more observations on the deacylation rates presented in Table XLIII appear worthwhile discussing.

TABLE XLIII
DEACYLATION RATES OF SOME NAPHTHALENE DERIVATIVES (355)

Naphthalene	k, min^{-1}	Rel rate
1-Acetamido	0.000033	~0.0041
2-Acetamido	0.000037	~0.0046
1-Acetamido-2-nitro	0.008	1
2-Acetamido-1-nitro	2.200	275
1-Acetamido-4-nitro	0.680	85
2-Acetamido-1,8-dinitro	>5.0	>625
1-Acetamido-4,5-dinitro	0.900	113
1-Acetamido-5-bromo-4-nitro	0.08	10

The reaction seems to proceed rapidly in the case of 2-acetamido-1,8-dinitronaphthalene (CXCVIIIb) and 1-acetamido-4,5-dinitronaphthalene (CXCVIIc). The mechanism responsible for such a high degree of activation does not seem to be clear, particularly because of the possible steric distortions in these molecules. In striking contrast to the above cases, 1-acetamido-8-nitronaphthalene (CXCVIIb) shows a remarkable resistance to deacylation; even after boiling it for 3 hr with sodium methoxide, the anilide is quantitatively recovered (355). In this case there is no resonance interaction of the nitro and amino groups but only steric hindrance due to *peri* interaction.

The reduction of carbonyl group reactivity in 1-ketonaphthalenes has been investigated by Kadesch (312) a number of years ago. He determined the percentage oximation of 1-acetylnaphthalene, 2-acetylnaphthalene, 1-acetyl-2-methylnaphthalene, and acetomesitylene and found them to be 46, 77, 1, and 2%, respectively, over a period of 10 hr. The slow reaction in the case of 1-acetyl- and 1-acetyl-2-methylnaphthalenes is obviously due to *peri* retardation.

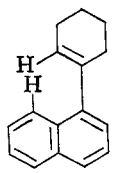
A comparison of the rates of perbenzoic acid oxidation of azonaphthalenes provides another illustration of the *peri* interaction. The data of Badger and Lewis (47) are given in Table XLIV. The relatively low reaction rate and the high heat of activation of 1,1′-azonaphthalene indicate considerable steric restrictions in the transition state for oxidation. Oxidation at either nitrogen in 1,1′-azonaphthalene would be impeded by *peri*-hydrogen, whereas in the other cases it should be easy to attack the nitrogen atom remote from the 1-naphthyl group.

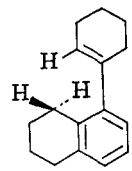
TABLE XLIV
RATES OF OXIDATION OF AZONAPHTHALENES WITH PERBENZOIC ACID AT 25° (47)

Compound	10^3k, l. $mole^{-1}$ min^{-1}	ΔH, kcal/mole
trans-Azobenzene	13.9	14.8
1-Phenylazonaphthalene	14.5	14.9
2-Phenylazonaphthalene	14.5	15.1
1,1′-Azonaphthalene	2.46	17.5
1,2′-Azonaphthalene	17.7	15.0
2,2′-Azonaphthalene	17.6	15.1

The acid-catalyzed exchange of *o*- and *p*-hydrogens for deuterium in aromatic tertiary amines is known to be subject to an *ortho* steric effect (107) since the transition state demands planarity of the dimethylamino group with the aromatic nucleus. On this basis, the prediction was made (107) that in 8-substituted 1-dimethylaminonaphthalene, the exchange rate would be considerably affected. Accordingly, there was no hydrogen–deuterium exchange in 8-nitro and 8-chloro compounds. However, experimental results suggested a 60% exchange for the even more hindered 1,8-bis-(dimethylamino)naphthalene (108). Polar effects may be responsible; a complete exchange is reported for 1,5-bis(dimethylamino)naphthalene.

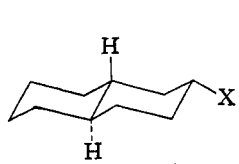
peri effects seem to affect the rates of catalytic hydrogenation of 1- and 2-cycloalkenylnaphthalenes (325, 337) and the coupling reactions of naphtholsulfonic acids with diazonium salts (593). The former reaction is known to proceed by a flatwise adsorption of the substrate on the catalyst surface (383), and as such any factor affecting the planarity of the substrate molecule would lead to slower hydrogenation. Klemm and Hodes (325) have found that 1-naphthylcyclohexene (CCI) is hydrogenated only half as fast as 2-naphthylcyclo-

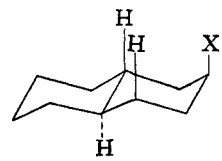

CCI

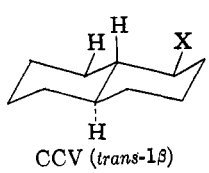

CCII

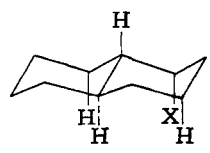
hexene. However, when the naphthalene ring is partially saturated as in CCII, addition of hydrogen is found to be fast. The reason for this is evident: the *peri*-methylene hydrogens are no longer in the same plane as the cyclohexenyl ring.

A brief mention about the fully saturated naphthalene derivatives would be appropriate in this section. In *trans*-1-α-decalyl derivatives, there will be three *syn*-axial interactions (two 1,3 and one 1,8 (as *peri*


CCIII (*trans*-2α)


CCIV (*trans*-2β)


CCV (*trans*-1β)


CCVI (*trans*-1α)

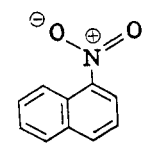
interactions), in contrast to only two interactions in the *trans*-2β isomer. Similarly the *trans*-1β isomer, though equatorial, has a 1,3-diaxial-like interaction (with the equatorial hydrogen at position 8), whereas the *trans*-2α isomer is free of this interaction. In many reactions, the reactivity of *trans*-1α form is much lower than those of the other isomers. For example, *trans*-1α-decalincarboxylic acid is esterified at the slowest rate compared to its isomers. Several other examples of this type are documented elsewhere (135, 183, 184, 253a).

2. *Studies Involving Only Qualitative Data*

a. Electrophilic Substitution in Naphthalene

In reactions of substituted naphthalenes, the position of entry of the incoming group is determined by the directive influence of the group already present and, equally important, the steric factor. The inherent preference of the naphthalene system for 1- over 2-substitution may also occasionally come into play. For example, sulfonation of 2,6- and 2,7-di-*t*-butylnaphthalenes occurs preferentially at the 4-position, the 1- and 3- positions being shielded in either ring (420). The direct introduction of two sulfonic acid groups at *peri* positions in naphthalene has not been possible, any such attempt resulting in 1,5 derivatives. The *peri* acid has, however, been prepared from 1,8-naphthylaminesulfonic acid (314).

The behavior of naphthalene derivatives on nitration presents a unique contrast to the above results. When 1-nitronaphthalene is nitrated, the product consists of a 1:2 mixture of the 1,5 and 1,8 isomers. This is attributed to what is called the "D-effect" (dipole effect) of the


CCVII

nitro group which is conducive to electrophilic attack at the adjacent *peri* position (578). Such an effect can be expected to operate in cationic attack. This view is substantiated by data obtained on nitration and bromination of N-acyl nitro-1-naphthylamines.

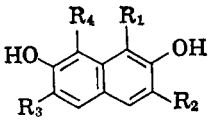
The ratio of 4 to 2 nitration of 5-nitro-1-acetnaphthalide is 2.6:1 while bromination leads to an even higher ratio. Other examples of preferential *peri* substitution may be found in the formation of 1,4,5-trinitronaphthalene from nitration of 1,5-dinitronaphthalene (566), of 4,5-dinitro-2-naphthol from nitration of 5-nitro-2-naphthol, of 1,8-dinitro-2-naphthol from 8-nitro-2-naphthol (64), and of 1,8-dinitro-2-methylnaphthalene from 1-nitro-2-methylnaphthalene (370). However, when 1-nitronaphthalene is nitrated with aqueous nitric acid, increasing amounts of the unhindered 1,5-dinitro isomer are formed. This is believed to be due to the increased bulk of the effective nitrating agent (solvated nitronium ion) which renders it incapable of reaching the *peri* position (566, 567). A similar reasoning would pre-

sumably apply to the results on the nitration of naphthalene with boron trifluoride–nitrogen tetroxide in nitromethane (34, 35). A reinvestigation of this reaction by Ward and Johnson (567) has, however, shown that the 1,8 to 1,5 ratio is 61:39, indicating fairly high yields of the 1,8 isomer despite the large size of the reagent.

Ionic bromination of 1-nitronaphthalene leads to 5- but not 8-bromination, perhaps due to the larger size of the reagent (bromonium > nitronium), thus manifesting a difference from nitration (567, 569). Molecular bromination of 5-nitro-1-acetnaphthalide leads again to 2-substitution, the attack at the *peri* position being sterically blocked. Also the "D-effect" suggested to explain the course of nitration could not hold for the neutral reagent here (569).

A comparison of the product ratio (4:2) for nitration of acetanilide and 1-acetnaphthalide indicates that under comparable conditions the 4:2 ratio is smaller for the naphthalene derivative than for the benzene analog. On electronic considerations alone, 1-acetnaphthalide should be expected to give a higher 4:2 ratio in view of the superior reactivity of naphthalene α positions. The orientation during nitration of 8-nitro-1-acetnaphthalide (277, 568) is also of interest. Here the ratio 4:2 is quite high. The reason for this appears to be a buttressing effect of the 8-nitro group on the 1-acylamino substituent which leads to formation of more of the 4 isomer at the expense of the less easily formed 2 isomer (568). The importance of buttressing effects in electrophilic substitution reactions in benzene derivatives has already been pointed out by Brown and McGary (104).

The orientation of halogen atoms introduced in chlorination and bromination of 2,7-dihydroxynaphthalene has been a matter of considerable dispute. Cooke, Johnson, and Owen (143) have observed that bromination of the 2,7-diol leads to 1,3- and 1,6-dibromo derivatives (CCVIII, $R_1 = R_2 = Br$, $R_3 = R_4 = H$; or CCVIII, $R_1 = R_3 = Br$, $R_2 = R_4 = H$) but not the 1,8-dibromo isomer in spite of the expected higher

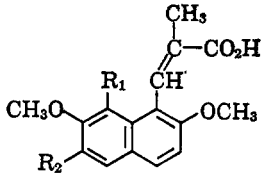


CCVIII

reactivity at 1- and 8-positions. These authors have expressed doubt regarding the reported isolation of 1,3,6,8-tetrabromo-2,7-dihydroxynaphthalene (CCVIII, $R_1 = R_2 = R_3 = R_4 = Br$) and its dimethyl ether, (65, 72, 73), especially since they observed that even the tribromo derivative of 2,7-naphthalenediol is unstable. Such a view is in accord with the failure (534) to obtain the 1,8-dibromo compound from 3,6-dicarboxy-2,7-naphthalenediol (CCVIII, $R_2 = R_3 = CO_2H$, $R_1 = R_4 = H$) or its dimethyl ether. However, Wilson (588) has upheld the claims of Bell (65, 72, 73) regarding the preparation of pure 1,3,6,8-tetrabromo 2,7-diol by direct bromination of the 2,7-diol. The reported failure to prepare this compound by halogenation is attributed to the prevalence of acidic reaction conditions which could lead to halogen migration. Indeed, Wilson (588) has carried out the bromination in the presence of sodium acetate, and the tetrabromo diol is found to be quite stable over a period of 3 years as revealed by constancy in melting point. Successful synthesis (72, 295) of the tetrabromo diol would seem to suggest that, despite steric inhibition to substitution, even bulky groups can be accomodated at the *peri* positions by slight molecular distortions (72).

Similar controversies exist in the earlier literature regarding other reactions. It has been reported (137) that chlorination of the 2,7-diol furnished the 1,8-dichloro compound. Bromination is also said to proceed likewise (510). Subsequently Ioffe and Federova (295) have reexamined bromination and suggested that the bromine atoms successively enter the 3-, then 3,6-, and finally the 3,6,8-positions. In contrast to this, Adams, Miller, McGrew, and Anderson (5) have assumed entry of bromine at 1- and 1,8-positions. A consideration of related reactions seems to justify Ioffe and Federova's orientation.

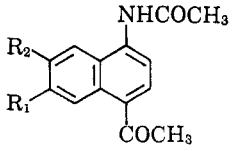
An erroneous assumption about the position of bromination of 2,7-dimethoxynaphthalene has led to failure in the projected synthesis of CCIXa with a view to resolve it. CCIXa was to be prepared from



CCIXa, $R_1 = Br$; $R_2 = H$
b, $R_1 = H$; $R_2 = Br$

1,8-dibromo-2,7-dimethoxynaphthalene which was believed to result from bromination of the ether. From what is now known of this reaction (587), the acid obtained from the dibromo ether (the 1,6 rather than the needed 1,8 derivative) could have been only CCIXb and not CCIXa; as is to be expected CCIXb has not shown optical activity.

The orientation of the incoming acyl groups during Friedel–Crafts acylation of naphthalene and its derivatives is also influenced by steric effects (44, 369). When 1,6- and 1,7-diacetylaminonaphthalene are acetylated, 4,7- and 4,6-diacetylamino-1-acetylnaphthalenes (CCXa and b) are the respective products. Thus in these cases, substitution does not occur at positions *ortho* or *peri* to the acetamido groups. In isomeric compounds where the reactive positions could be only



CCXa, $R_1 = NHCOCH_3; R_2 = H$
b, $R_1 = H; R_2 = NHCOCH_3$

ortho or *peri* as in 1,4, 1,5, and 2,7 derivatives, no acetylation is found to occur (369).

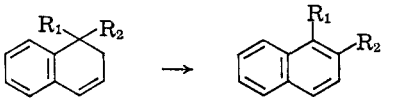
Baddeley (44) has investigated the acylation of naphthalene itself. Almost pure 1-ketones are obtained when acyl chloride and aluminum chloride are used for acylation in solvents like methylene chloride or ethylene chloride. When, however, nitrobenzene is used as solvent, almost exclusive β substitution is observed. This is plausibly due to the increased bulk of the acylating agent in nitrobenzene solution. The α position is not accessible to attack with such bulky reagents. Consequently, the more readily accessible β position is the target of attack. Gore and Hoskins (239) have made similar observations in acylation of anthracene. In nitrobenzene solution, anthracene affords only a mixture of 1- and 2-acetylanthracenes on treatment with acetyl chloride. Even when 9-acetylanthracene is formed under controlled conditions, the *meso*-acetyl group is found to be quite labile (239). In contrast to this, the *meso*-benzoyl group in 9-benzoylanthracene is quite stable under comparable conditions. The larger size of the acetyl group is advanced as a likely reason for this behavior (105, 302).

More recently, Alcorn and Wells have studied the nitration of 1- and 2-methylnaphthalenes (9a) and 1- and 2-methoxynaphthalenes (9b). Nitration of 1-methylnaphthalene in acetic acid yields an unexpectedly large amount of the *peri*-nitro compound, apparently owing to some specific *peri* activation. The order of activation for 2-methoxynaphthalene is 6 > 1 > 8. On theoretical considerations, the 1-position would be expected to be more reactive than the 6-position. This reversal is presumably due to the inductive effect of the 2-methoxyl group acting at the 1-position as well as steric hindrance to attack at that position.

b. Rearrangements in the Naphthalene Series

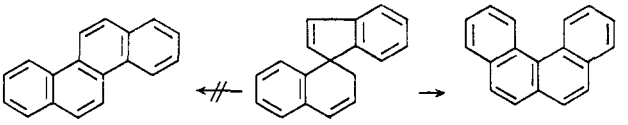
Several reports concerning the isomerization of 1-alkyl and aryl substituents to the less hindered 2-position in naphthalene have appeared in the literature. Mayer and Schiffner (414) and Cullinane and Chard (152) have employed catalysts at high temperatures to bring about the isomerization of 1-methyl and 1-phenyl groups. Tsukervanik and Terent'eva, however, claim (552) that the reaction proceeds by merely heating the 1 isomer without any catalyst. In view of these reports, the nonisomerization (293) of the apparently hindered 1-*t*-butylnaphthalene is surprising. In some cases, heating an α-alkylated naphthalene leads to loss of α substituents, thereby relieving steric strain in the molecule. A summary of such examples is available (138).

More recently, Herz and Caple (268) have studied the migratory aptitudes of R_1 and R_2 in CCXI to give CCXII on treatment with chloranil in boiling toluene.



CCXI CCXII

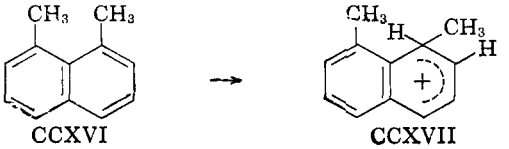
Thus CCXI (R_1 = Me; R_2 = CH=CH_2) affords 27% of 1-methyl-2-vinylnaphthalene (CCXII, R_1 = Me; R_2 = CH=CH_2). There is no evidence of methyl migration. With CCXI (R_1 = C_6H_5; R_2 = CH=CH_2), 1-phenyl-2-vinylnaphthalene is the product involving again a vinyl migration. In CCXIII also, styryl migration leading to CCXIV seems to be preferred over phenyl migration which would lead to



CCXV CCXIII CCXIV

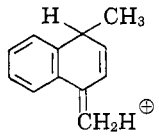
CCXV. The relative ease of migration seems to be methyl < phenyl < styryl ≈ vinyl. Though steric factors may facilitate these reactions, they do not seem to control the outcome; if they did, the bulkier group would be expected to migrate.

The isomerization behavior of dimethylnaphthalenes has been studied by Suld and Stuart (532). The migration is slow for all the isomers except 1,8- and (to a lesser extent) 1,4-dimethylnaphthalene. Employing only hydrogen fluoride, 98% of the 1,8 compound is found to isomerize to the 1,7 isomer in 10 min at room temperature. The other isomers require a boron trifluoride catalyst for isomerization; under these conditions 1,4-dimethylnaphthalene rearranges (to 1,3-) much faster than any of the other isomers. Rearrangement of the 1,5 isomer is not accelerated. Alkyl migrations of this type in the benzene series are known to proceed by an initial addition of proton followed by a 1,2-methyl shift (415). The unusual ease of rearrangement of the 1,8 isomer may be explained on the basis of a steric *peri* interaction in the ground state which is, to a large extent, relieved in the transition state (resembling the σ-complex intermediate). Whether a similar explanation applies to the 1,4 isomer is doubtful in view of the lack of acceleration in the rearrangement of the 1,5 isomer. Of course, electronic effects are



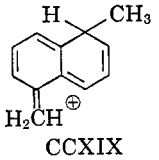
CCXVI CCXVII

also very important in alkyl migrations, as is well known in the alkylbenzene series and may well account for the difference in behavior between the 1,4 and 1,5 compounds.



CCXVIII

canonic for the σ complex from the 1,4 isomer



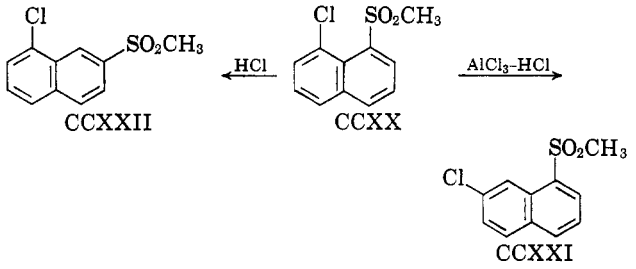
CCXIX

canonic for the σ complex from the 1,5 isomer

The isomerization of *peri*-dihalonaphthalenes has also been studied. Armstrong and Wynne (18) have observed that 1,8-dichloronaphthalene rearranged to the 1,5 isomer on heating with hydrochloric acid at 290°. 1,8-Dibromonaphthalene is, however, observed to isomerize to the 1,7-dibromide when heated with β-naphthalenesulfonic acid (352). When 1-chloro-8-bromonaphthalene is subjected to this reaction, the bromine atom migrates to give 1-chloro-7-bromonaphthalene. The nonisomerization of 1,7-dibromonaphthalene indicates the irreversibility of the reaction. The ease of isomerization of the *peri* derivatives is stated to be in the order 1,8-dibromo > 1,8-chlorobromo > 1,8-dichloro (352) as indicated by the extent of isomerization observed in each case in a given period of time shorter than that needed to establish equilibrium.

Other *peri*-dihalogen compounds like 1,8-dichloronaphthalene-3-sulfonic acid and 1,8-dibromo-2,7-dihydroxynaphthalene also isomerize smoothly to less hindered compounds in the presence of protonic acids (18, 142). Migration of halogen atoms is known with mono- and dihalonaphthalenes even with non-*peri*-halogens, but in these cases the presence of a catalyst seems to be necessary. The relative ease of migration in *peri* derivatives is suggested to be a consequence of steric effects (348). When the *peri* substituents emerge from the plane of the naphthalene ring, the bond geometry around the *peri*-carbon atom would tend to become tetrahedral. As already mentioned, such a process facilitates the formation of an activated complex resulting from proton attack.

peri-Halonaphthyl methyl sulfones are also known to undergo such migration. On heating methyl 8-chloro-1-naphthyl sulfone with concentrated hydrochloric acid at 200° for 5 hr, methyl 1-chloro-7-naphthyl sulfone is obtained in 40% yield. A similar isomerization is reported with the ethyl but not with the benzyl sulfone (348). The presence of an acid is essential for the migration as shown by the failure of methyl 8-chloro-1-naphthyl sulfone to rearrange on heating it with 30% sodium chloride solution at 200°. The migration of groups also depends on the reaction conditions. Thus in presence of 2 moles of aluminum chloride and dry hydrogen chloride, the *peri*-chloro sulfone isomerizes to a mixture of methyl 2-chloro-8-naphthyl sulfone and methyl 1-chloro-7-naphthyl sulfone in which the former product predominates (351). In contrast, the use of hydrochloric acid is shown to cause migration of the methyl sulfonyl group and not the halogen. This difference in behavior is attributed to the formation of a



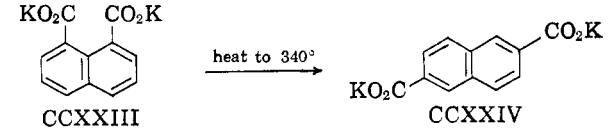
CCXXII CCXX CCXXI

complex between the sulfonyl group and aluminum chloride rendering the sulfone-bearing carbon atom inaccessible to proton attack which is an essential step in the reaction. The migration of halogen atom is, however, not inhibited, since the halogen-bearing carbon atom is free to accept a proton. This view is supported by the observation that when less powerfully coordinating catalysts like ferric chloride and zinc chloride are employed, the methyl sulfonyl group does migrate more extensively (349, 351).

The thermal isomerization of methyl 1- or 2-naphthyl sulfone in presence of zinc chloride leads to an equilibrium mixture containing about 96–97% of the 1-sulfone. In *peri*-halo sulfones, the isomerization is irreversible, presumably because of the lability of the 1,8-disubstituted compound. Non-*peri*-halo sulfones like 1,4, 1,5, 2,5, and 2,8 isomers also undergo rearrangement, but in these cases the reaction proceeds much slower than with methyl 1-naphthyl sulfone and in a reversible fashion in contrast to the *peri* isomer which is found to rearrange faster than methyl 1-naphthyl sulfone irreversibly (235, 348). Mention may also be made that phenyl 1-naphthyl sulfone also rearranges to an equilibrium mixture of 1 and 2 isomers on heating with zinc chloride–hydrogen chloride (235).

A similar irreversible migration of halogen from the 8- to 7-position occurs on heating 8-chloro-1-naphthoic acid at 150° for 1 hr with a melt of aluminum chloride–sodium chloride (345). Isomerization of the non-*peri*-5-chloro-1-naphthoic acid to a mixture of 5- and 6-chloro acids is reversible. The irreversible conversion of 8-chloronaphthalene-1-sulfonic acid to the 7-chloro isomer has also been accomplished (345).

Migration of carbonyl groups from *peri* positions has also been recorded. When the dipotassium salt of naphthalic acid is heated above 340° under anhydrous

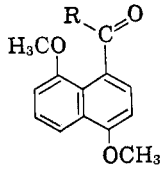


CCXXIII CCXXIV

conditions in a carbon dioxide atmosphere, the 2,6 isomer is obtained (264), again indicating a preference for the loss of *peri* interaction.

c. Reactions of Naphthyl Ketones and Naphthyl Grignard Reagents

The reactivity of the carbonyl group in aliphatic, alicyclic, and aromatic ketones is a function of the steric and electronic properties of the groups bonded to the carbonyl carbon. For example, the normal carbonyl reactivity is considerably diminished in hindered aromatic ketones. In naphthalene derivatives, reactions of 1-naphthyl ketones are found to be influenced by the *peri* substituent. Evidence presented in other sections of this review indicates that the 1-carbonyl group is twisted out of the plane of the naphthalene ring. Thus it is found (120) that 4,8-dimethoxy-1-naphthyl methyl ketone (CCXXVa) fails to undergo the Pfitzinger reaction with isatin. Poor yields have also been reported (121) in the reaction of 5,8-dimethyl-1-tetralone with isatin. On the other hand, the formyl group in 4,8-dimethoxy-1-formylnaphthalene (CCXXVb) behaves normally in condensing with benzyl cyanide. Suppression of carbonyl group reactivity has also been noticed in the failure of 1,8-di(*n*-hexanoyl)naphthalene to yield a crystalline 2,4-dinitro-

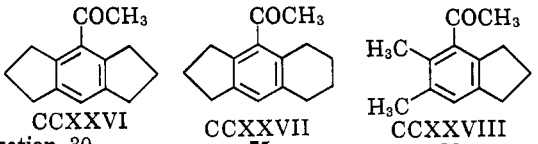


CCXXVa, R = CH_3
b, R = H

phenylhydrazone (57), and of 8-benzhydryl-1-naphthyl methyl ketone to yield a hydrazone or dinitrophenylhydrazone (374). Kadesch (312) has also reported the slow rate of oximation of 2-methyl-1-naphthyl methyl ketone. No reference appears to have been made to carbonyl derivatives of 2-methoxy-1-acetylnaphthalene. In contrast to these examples, the keto methyl group in CCXXVa, being free of steric effects, readily condenses with *p*-anisaldehyde to form chalcones.

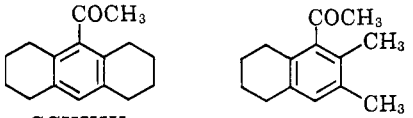
A number of studies have been reported on the reactions of 1-naphthyl Grignard reagents with carbonyl compounds, or of 1-ketonaphthalenes with alkyl and aryl Grignard reagents. For example, Illingworth and Peters (293) have attempted to prepare 1-*t*-butylnaphthalene from 1-tetralone and *t*-butylmagnesium chloride followed by dehydration and dehydrogenation. This was not successful presumably due to steric effects. Similarly methyl 8-benzhydryl-1-naphthoate also fails to react with phenylmagnesium bromide even after boiling for several hours (590).

The Grignard reaction of methylmagnesium iodide with a series of ketones CCXXVI–CCXXX has been studied with a view to assess the dependence of steric effect on ring size (23). Both enolization and addition



CCXXVI CCXXVII CCXXVIII

	CCXXVI	CCXXVII	CCXXVIII
% enolization	30	75	93
% addition	70	25	7

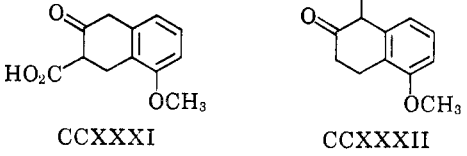


CCXXIX CCXXX

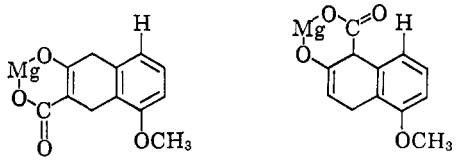
	CCXXIX	CCXXX
% enolization	95	100
% addition	5	0

reactions occur, but the extent of addition reaction decreases with increasing steric bulk of the hindering substituents. A parallel observation made with regard to hypochlorite oxidation of the above ketones (21, 23) may be mentioned here. While CCXXVI could be smoothly oxidized to the carboxylic acid, CCXXVII and CCXXVIII gave a mixture of trichloromethyl ketone and the acid, and CCXXIX and CCXXX furnished only the trichloro ketone. Hypochlorite oxidation of 2-methoxy-1-acetylnaphthalene also stops at the chloro ketone stage (224).

Pelletier and Parthasarathy (473) have observed that 5-methoxy-2-tetralone reacts with methylmagnesium carbonate to give the β-keto acid CCXXXI rather than CCXXXII. The likely reason for this is suggested to be the greater ease of formation of the necessary



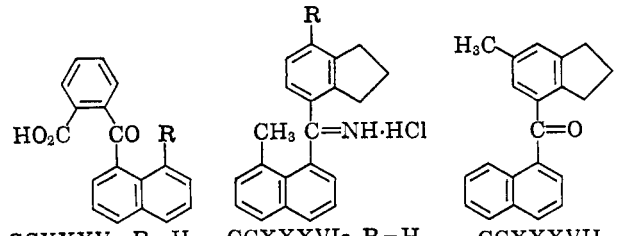
CCXXXI CCXXXII



CCXXXIII CCXXXIV

intermediate CCXXXIII over CCXXXIV. It is also of interest to note that formylation of β-tetralone occurs at the 1-position but oxalylation prefers the 3-position (520).

Fieser and Seligman (204) have studied the addition of methylmagnesium halide to the keto acids CCXXXVa and CCXXXVb (and their ethyl esters). The addition reaction is found to proceed in good yield with CCXXXVa but not with the *peri*-methyl acid



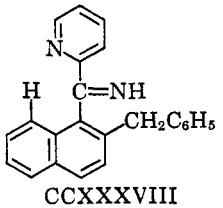
CCXXXVa, R = H
b, R = CH_3

CCXXXVIa, R = H
b, R = CH_3

CCXXXVII

CCXXXVb; in the latter only unsaponifiable oils could be obtained.

The ketimine salt from *o*-chlorobenzonitrile and the Grignard reagent from 8-methyl-1-bromonaphthalene is found to resist hydrolysis. Hydrolysis could, however, be accomplished by using a mixture of sulfuric and formic acids at 150° in a sealed tube (204). Similarly, the ketimines CCXXXVIa and b were formed in poor to moderate yield from the appropriate reagents but could not be hydrolyzed to the ketones even under those conditions which worked well for the *o*-chlorophenyl derivative. These results are in striking contrast to the 94% yield of the ketone CCXXXVII obtained from 1-naphthylmagnesium bromide and 4-cyano-6-methylhydrindene (207). Vingiello and Delia (559) have observed that 2-benzyl-1-naphthyl 2-pyridyl ketimine (CCXXXVIII) could not be successfully hydrolyzed to the ketone by the usual procedure.



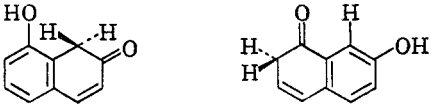
CCXXXVIII

When drastic conditions are used, more complex changes than simple hydrolysis were found to occur. The hydrolysis is made difficult presumably by hydrogen bonding between the imino nitrogen and pyridine nitrogen and also by steric hindrance to rear side attack at the imino group. The expectation that such effects should vanish with 3- and 4-pyridyl isomers of CCXXXVIII is realized by their smooth hydrolysis to the ketones (559).

The reaction of unhindered esters with Grignard reagents generally leads to tertiary alcohols *via* ketones. With 1-naphthylmagnesium bromide and aliphatic carboxylic esters, the product is found to be a mixture of alkyl 1-naphthyl ketone and α,α'-di(1-naphthyl)ethylene and very little, if any, of the tertiary alcohol (476). One may interpret the results to indicate that in order to escape unfavorable steric situations, the carbon atoms attached to α-naphthyl group prefer an sp^2 state (ketone or olefin) to an sp^3 state (tertiary alcohol).

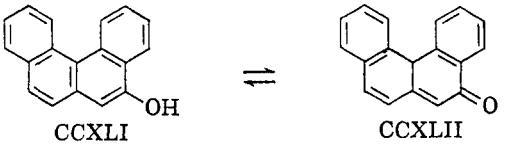
Sunthankar and Gilman (533) have noticed that 1-lithio-2-hydroxynaphthalene did not react with triphenylsilyl chloride, though it reacted with trimethylsilyl chloride. The isomeric 4,1- and 6,2-naphthalenes react readily to form the chlorosilanes.

Results obtained with Bucherer reaction of naphthols (498) and benzo[*c*]phenanthrols (451) are also considered in this section since an essential step in the Bucherer reaction is the ketonization of the phenol. When 1,7-naphthalenediol is heated at 130–180° with aqueous methylamine, 7-methylamino-1-naphthol is formed. The initial ketonization of the diol can proceed to give either CCXXXIX (leading to 7-methylamino-1-naphthol) or CCXL (leading to 8-methylamino-2-naphthol). Which of the two will be formed is presumably determined by the magnitude of the relief of strain in going from the substrate to the intermediate. The product formation may be rationalized by the fact that steric strain relief is greater in CCXXXIX than in



CCXXXIX CCXL

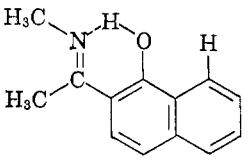
CCXL. All the steps involved in the reaction, *viz.* ketonization, addition of the amine, and rearomatization, will be sterically retarded in CCXL. Newman and Blum (451) have found that 1- and 2-hydroxybenzo[*c*]phenanthrenes are converted to the amines by the Bucherer reaction. This would suggest the presence of keto forms of the phenols in equilibrium with the enol form. The equilibrium may be expected to shift to the keto form in 5-hydroxybenzo[*c*]phenanthrene



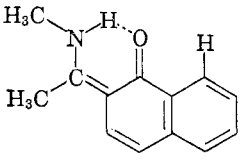
CCXLI ⇌ CCXLII

in view of the possible strain relief ($sp^3 \rightarrow sp^2$). However, no evidence of ketonic form could be obtained by infrared methods (451). Ullmann and Buncel (555) report another related example. In these cases, one has to weigh the energy gain from an $sp^3 \rightarrow sp^2$ process with the reduction in resonance energy by loss of aromaticity.

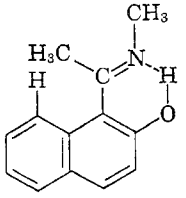
Dudek (175) has investigated the structure of the N-methylimines derived from 1-hydroxy-2-acetyl- and 2-hydroxy-1-acetylnaphthalenes. The relative stability of the keto amine *vs.* the hydroxy imine forms is governed by steric factors since hydrogen bonding stabilizes both forms. Thus the keto amine structure CCXLIV is more stable than the phenol imine structure CCXLIII while, for the derivative from 2-hydroxy-1-acetylnaphthalene, the hydroxy imine form CCXLV is more favored than CCXLVIa. This is because of the fact that in CCXLV the unfavorable steric strain may be relieved by a twisting of the imino



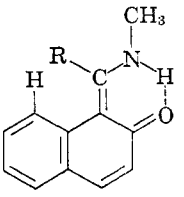
CCXLIII



CCXLIV



CCXLV



CCXLVIa, R = CH_3
b, R = H

acetyl group about the C–C bond which is not possible in CCXLVIa. (This rotation would, however, be opposed by hydrogen bonding forces.) In CCXLVIb (derived from 1-formyl-2-naphthol), involving as it does only a smaller steric interaction, the keto amine form is stable. However, the differing resonance energy of the naphthalene nucleus by a shift from benzenoid to quinoid structure may perhaps be a complicating factor in the foregoing arguments.

d. Lability of Substituents in *peri*-Naphthalenes

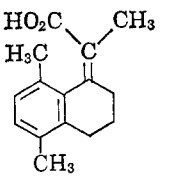
The presence of a carboxyl group *peri* to a nitro or halo substituent in naphthalene seems to exert a labilizing effect on the latter substituents. This has been studied in an early series of investigations. When 8-nitro-1-naphthoic acid is treated with thionyl chloride or bromide, the nitro group is displaced by the halogen. The lability of the nitro group seems to be associated with *peri* effects since no such displacement is observed with 5-nitro-1-naphthoic acid. The nitro group in *o*-nitrobenzoic acid is also inert under comparable conditions (499).

The halogen atoms in *peri*-halonaphthoic acids are found to be easily replaced by alkoxy or aryloxy groups (503). They can be dehalogenated by heating them with copper–bronze in boiling toluene. Under these conditions non-*peri* and non-*ortho*-nitro and halo substituents are usually unaffected. In contrast to the normal behavior of carboxylic acids, the *peri*-halo acids cannot be decarboxylated by the copper–quinoline procedure (502). The *peri*-bromo acids are found to be as reactive as *o*-iodobenzoic acids toward nucleophilic attack by alkoxy and aryloxy groups. However, when the reagent is bulky (*e.g.*, sodium malonate, sodium iodide, or silver nitrite), the reaction with 8-bromo-1-naphthoic acid is found to be slow, presumably because of the crowded transition state that would result (500).

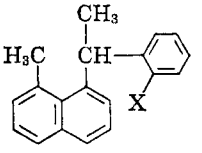
Hodgson and Crook (278) have examined the reactivity of 1,8-nitrochloronaphthalene with copper–bronze and found that the reaction proceeds in good yields to give 8,8′-dinitro-1,1′-binaphthyl. Earlier Salkind (506) has concluded from similar studies on several heteronuclear nitrohalonaphthalenes that activation of halogen by heteronuclear nitro group is not significant. He has not, however, studied the *peri*-halo compound in which case the observed reactivity may arise from the special proximity of the substituents.

e. Miscellaneous Reactions

The difficulties encountered in the esterification and hydrolysis of hindered acids, phenols, and their derivatives are well known. Among naphthalene derivatives, several such examples are reported. Thus, Fischer esterification of 2-substituted 1-naphthoic acids cannot be accomplished (74, 422, 423). On the other hand, 3-chloro- and 3-hydroxy-2-naphthoic acids are esterified by this procedure in high yield. Failure to esterify 8-bromo- and 8-chloro-1-naphthoic acids has also been recorded (181, 499). Newman and Hussey (443) have reported that the acid CCXLVII resists esterification. Comparable to these results is the hydrolysis of the



CCXLVII



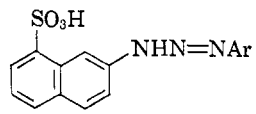
CCXLVIIIa, X = CN
b, X = $CONH_2$

nitrile CCXLVIIIa (potassium hydroxide, reflux, 250 hr) or the corresponding amide CCXLVIIIb (potassium hydroxide, reflux in ethylene glycol, 10 hr) (129). O'Brien and Smith (456) could obtain the aryloxyacetic acid from 2-chloro-1-naphthol and chloroacetic acid only in small yields. However, the reaction proceeds smoothly with the more reactive ethyl bromoacetate.

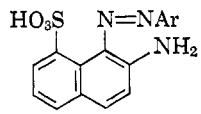
The reactions of some naphthylamines have also indicated certain anomalies which are attributed to *peri* effects. Ward and Day (565) have found that 2,4,8-trinitro-1-naphthylamine does not complex with picric acid or 2,3,4-trinitrotoluene nor does it react with 2,4-dinitrochlorobenzene or *p*-nitrobenzaldehyde. The nitroamine was also found to undergo acetylation only with difficulty and diazotization proceeded very slowly, requiring 12 hr for completion. The amine could be converted to the chloro or bromo compound only in low yields, and the iodo compound could not be prepared at all. The marked reduction in the reactivity of the trinitroamine is unique since the related derivative 2,4-dinitro-1-naphthylamine is quite reactive toward the reagents indicated above.

Quaternary salt formation of tertiary aromatic amines is also found to be affected by steric effects. Thus N,N-dimethyl-*o*-xylidine and 5,6,7,8-tetrahydro-1-dimethylaminonaphthalene do not form quaternary salts on treatment with methyl iodide. 7-Dimethylaminoindan does form the quaternary salt, however.

Diazo coupling reactions of naphthylaminesulfonic acids have been studied by Smith (518). 2-Naphthylamine-8-sulfonic acid reacts with arenediazonium salts to give more of the diazoamine CCXLIX (attack at



CCXLIX

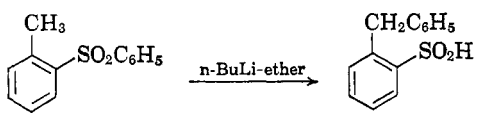


CCL

nitrogen) than the azo compound CCL (attack at the nucleus). With 2-dimethylaminonaphthalene-8-sulfonic acid, no coupling reaction is reported. Similar dampening of the coupling and bromination reactions is witnessed in hydroxynaphthalenesulfonic acids also (518).

A few examples are on record (116, 285) suggesting the operation of *peri* effects in the addition of bases to 1,2-naphthyne. The product obtained from these reactions is often a mixture of 1- and 2-substituted naphthalenes. The amount of the 1-substituted isomer in the mixture decreases with the increase in the size of the reagent, presumably owing to steric hindrance to attack at the 1-position.

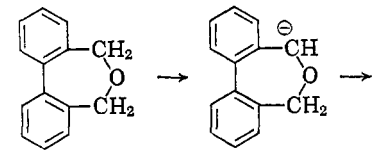
Truce and Hampton (551) have found that *o*-methylbiphenyl sulfones rearrange to *o*-benzylbenzenesulfinic acids in presence of butyllithium in ether. On



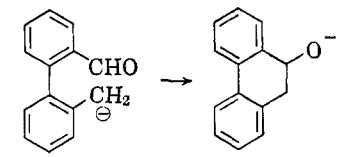
CCLI CCLII

subjecting methyl-1-naphthyl phenyl sulfones to this rearrangement, the ease of reaction is found to be in the order 2-methyl-1-naphthyl phenyl sulfone > 8-methyl-1-naphthyl phenyl sulfone. This is believed to indicate a smaller steric acceleration of the reaction by *peri*-methine than by an *o*-methyl group though, in view of the difference in the ring size of the quasi-cyclic transition state, the two cases may not be strictly comparable. The above authors also report that the conversion of 8-benzyl-1-naphthalenesulfinic acid to the chloromercuri derivative requires more vigorous reaction conditions (2 hr, 70–80°) than needed for the non-*peri* isomers.

Diphenan (CCLIII) and benzyl phenyl ether, $C_6H_5CH_2OC_6H_5$, are known to rearrange to alcohols on treatment with potassium amide in liquid ammonia. The reaction is said to proceed through the intermediate formation of the anion CCLIV (as illustrated for diphenan) followed by intramolecular addition of the anion to the carbonyl group. In the case of related compounds such as 2,5-dihydrofuran, phthalan, and 1,8-naphthalan, this rearrangement could not be accomplished (573). The nonoccurrence of the reaction

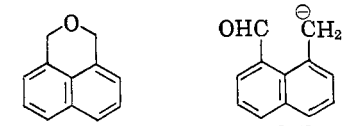


CCLIII CCLIV



CCLV CCLVI

with naphthalan (CCLVII) is attributed to suppression of resonance stabilization of the anion intermediate

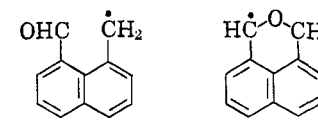


CCLVII CLVIII

CCLVIII due to steric hindrance (283). Huang and Lee (283) have investigated the somewhat similar radical rearrangement of benzyl ethers initiated by *t*-butoxy radicals. Depending upon the stability of the intermediate radical, there can be either disproportiona-

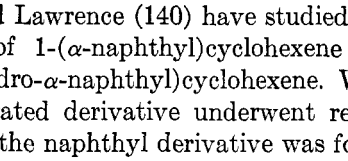
$$ArCH_2OR \longrightarrow ArCHOR \longrightarrow ArCHO + R\cdot$$
$$\downarrow$$
$$(ArCHOR)_2$$

tion or dimerization. The reaction with 1,8-naphthalan is found to yield only iso- and *n*-bisnaphthalan (dimerization product from CCLIX) but not the product excpected from the radical CCLX.



CCLX CCLIX

Cook and Lawrence (140) have studied the catalytic reduction of 1-(α-naphthyl)cyclohexene and 1-(5,6,-7,8-tetrahydro-α-naphthyl)cyclohexene. While the partially saturated derivative underwent reduction with great ease, the naphthyl derivative was found to resist reduction. The planar *peri*-hydrogen in CCLXI presumably offers more hindrance to reduction at the double bond than the nonplanar methylene system in CCLXII.

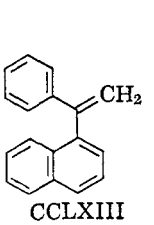


CCLXI CCLXII

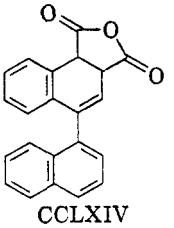
Failure to successfully oxidize 4-nitro-1,8-dimethylnaphthalene to the corresponding naphthalic acid using chromic anhydride–acetic acid or potassium perman-

ganate–pyridine is also attributed to *peri* effects. Employing a variety of reaction conditions, it is found that this compound either does not undergo oxidation or extensively resinifies (158). This is comparable to the behavior of *o*-dialkyl derivatives during oxidation. It is worthy of note that the sterically related derivative 5-nitroacenaphthene undergoes oxidation to 5-nitronaphthalic anhydride smoothly with chromic acid. It is, however, surprising to note that *peri* orientation of the substituents in many polycyclic nitro derivatives imparts photosensitivity to these molecules. Thus the *peri*-nitro derivatives 1,8-nitronaphthalenesulfonic acid, 1,8-nitromethylnaphthalene, and 1,9-nitroanthracenesulfonic acid are quite photosensitive showing signs of decomposition when exposed to light, whereas their non-*peri* isomers are relatively more stable (524).

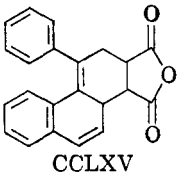
The Diels–Alder addition of 1-naphthylacrylic acid to butadiene and 2,3-dimethylbutadiene has been effected (517). The addition proceeds only when the reactants are heated at 150–190° for several hours in an autoclave; with cinnamic acid, the reaction proceeds at relatively lower temperature. The more stringent conditions in the case of naphthalene derivatives is probably due to steric effects that are not present in cinnamic acid. A similar steric restriction probably obtains in the reaction of 1-phenyl-1-(α-naphthyl)-ethylene (CCLXIII) with maleic anhydride (536). CCLXIII may be expected to react as 1-vinylnaphthalene rather than as styrene from a knowledge of the re-



CCLXIII



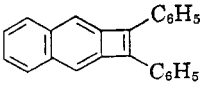
CCLXIV



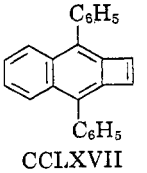
CCLXV

activity of these systems. However, the product obtained from the reaction suggests that the reaction occurs preferentially involving the styrene moiety (giving CCLXIV) but not the vinylnaphthalene system (in which case, the product should be CCLXV). It is perhaps of interest to note that 1,1-di(α-naphthyl)-ethylene is quite inert toward maleic anhydride (536).

Cava, Hwang, and Van Meter (131a) have reported a successful synthesis of the cyclobutadiene derivative CCLXVI, but all attempts to prepare the nuclear



CCLXVI



CCLXVII

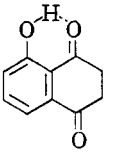
phenyl-substituted analog CCLXVII have failed. This observation is rationalized by invoking the stabilization of CCLXVI by phenyl group resonance in this system which may be significantly reduced in CCLXVII because of the nonplanarity of the phenyl groups in the latter (131). The fact that the phenyl groups are attached to the six-membered ring in CCLXVII, but to the four-membered ring in CCLXVI, may, however, be the decisive factor here.

Homolytic methylation of naphthalene has been effected using di-*t*-butyl peroxide, and the ratio of α- to β-methylnaphthalenes has been determined under different experimental conditions. The results are interpreted in terms of steric hindrance to α substitution and the intrinsic polarizability differences between the α- and β-positions (321).

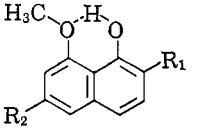
C. HYDROGEN BONDING IN NAPHTHALENE DERIVATIVES

Among naphthalene derivatives, intramolecular hydrogen bonding is possible in suitably substituted 1,2, 2,1, 2,3, and 1,8 derivatives. In 1,8 derivatives, the chelate ring is formed across the *peri* positions. Hydrogen bonding in 1,2 and 2,1 derivatives is found to be considerably influenced by the steric effect of the *peri* substituent. The extent of such hydrogen bonding in these compounds has been studied by the use of infrared, ultraviolet, and nuclear magnetic resonance methods. Differences in chemical reactivity have also been used to examine the stability of the chelates.

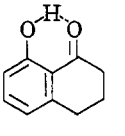
The ease with which a hydroxyl group reacts with diazomethane or phenyl isocyanate may be expected to provide an indication of the extent of intramolecular hydrogen bonding between an OH and carbonyl group. A hydrogen-bonded hydroxyl reacts either sluggishly or not at all in ether solution. In hydroxylic solvents, however, intramolecular hydrogen bonding is extensively broken down, thereby increasing the reactivity of the free hydroxyl. However, if the compound is strongly hydrogen bonded as in β-hydrojuglone (CCLXVIII) (541), 8-methoxy-1-naphthol (CCLXIXa) (100), 2,8-dimethoxy-6-methyl-1-naphthol (CCLXIXb)



CCLXVIII



CCLXIX, a, $R_1 = R_2 = H$
b, $R_1 = OCH_3$; $R_2 = CH_3$



CCLXX

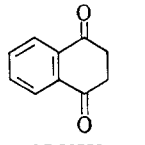
(100), and 8-hydroxy-1-tetralone (CCLXX) (193), there is no reaction in either ether or alcohol. In contrast, 8-arylsulfonyl-1-naphthols reacted readily with diazomethane even in ether solution (512) indicating chelation in *peri*-hydroxy sulfones to be weak, if not absent. The behavior of *o*-hydroxy sulfones is also similar.

A comparison of the behavior of *ortho*- and *peri*-substituted naphthols on methylation has also been

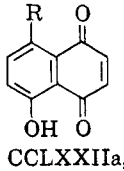
made (100). The results indicated that a six-membered chelate ring in *peri* derivatives such as 4,8-dimethoxy-1-naphthol is stronger than a five-membered chelate ring in the corresponding *ortho* derivatives. The O–H $\cdots$O distance of 2.60 A needed for facile chelation is said to obtain in β-diketones, *o*-nitrophenols, and *peri*-substituted hydrocarbons. A five-membered chelate ring with this O–H$\cdots$O distance would be strained, and hence the hydrogen bond would be much weaker (271). It must, however, be pointed out that the reactivity of hydroxycarbonyl compounds toward diazomethane or phenyl isocyanate may not provide a very reliable index of intramolecular hydrogen bonding (193).

Perekalin and Segalina (474) have attributed the insolubility of 8-phenylazo-1-naphthol in alkali to hydrogen bonding in this molecule which reduces the acidity of the phenolic hydrogen. In contrast, the non-*peri*-hydroxy compounds do dissolve in alkali. Furthermore, the ultraviolet spectra of *peri*-phenylazonaphthol do not vary in neutral and alkali solutions. One would normally expect a bathochromic shift in the ultraviolet region on passing from the free phenol to the phenoxide ion.

The mode of reduction of juglones is influenced by hydrogen bonding in the *peri* derivatives (541). For example, CCLXXI is reduced to the dihydroxy compound with stannous chloride and acid. However, the monohydroxyquinone CCLXXIIa under the same conditions is reduced to dihydro dione but not to the diol. The reduction of CCLXXIIb to the corresponding dione proceeds with even greater ease. In the latter cases, the observed reaction course is presumably due to stabilization of the product by chelation.

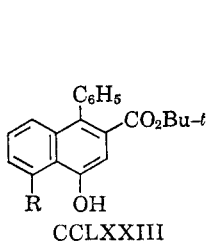


CCLXXI

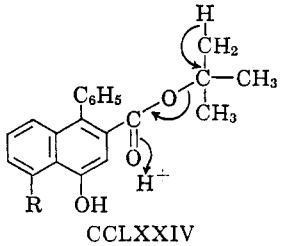


CCLXXIIa, R = H
b, R = OH

On heating *t*-butyl 4-hydroxy-2-naphthoates (CCLXXIII) alone at 190–225° for about 15 min, isobutene is evolved and a 90% conversion to 2-naphthoic acids is observed (334). Under the same conditions, esters having such *peri* substituents which can hydrogen-bond with the hydroxyl group are recovered unchanged. In presence of free phenols, however, the reaction does occur, indicating that the reaction involves catalysis by the phenolic hydrogen. The lack of reactivity of certain *peri*-substituted esters in the absence of external acidic catalysts is presumably due to the nonavailability of the phenolic proton owing to internal hydrogen bonding.



CCLXXIII



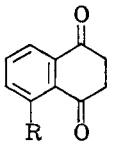
CCLXXIV

A more qualitative approach to *peri* effects on intramolecular hydrogen bonding has been attempted by using the wet and dry melting point method (54, 133). This method depends on the observation that the difference between the melting point of an organic compound when wet with water and when dry is much less for a chelated molecule than found for the corresponding nonchelated isomer. For example, among the nitroacetnaphthalides, there is a large difference (33–46°) between the wet and dry melting points of 2,1, 4,1, and 8,2 isomers (indicating absence of internal hydrogen bonding); in 1-nitro-2-acetamidonaphthalene this difference is only 13–14° (indicating chelation). This observation is also suggested to reveal a larger steric effect of the *peri*-hydrogen on the 1-acetamido group than on the 1-nitro group, leading to an out-of-plane twisting (and suppression of chelation) in 1-acetamido-2-nitronaphthalene but not in the 1-nitro-2-acetamido analog. Among acetylnaphthols, the wet and dry melting point method does not seem to be sensitive enough to assess the relative degree of hydrogen bonding in the *ortho* derivatives (133). No data seem to be available as to whether or not 1,8-acetylnaphthol is hydrogen-bonded. Chelation, if at all present, in 1,8-acetylnaphthol may be expected to be weak in view of the unfavorable chelate ring size.

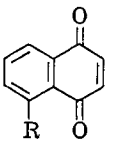
More precise studies of hydrogen bonding in *peri*-substituted naphthalenes have been made utilizing infrared methods. The compounds studied include hydroxycarbonyl compounds (62, 282, 286, 288), polyhydroxynaphthalenes (100, 282, 334), nitronaphthols (392), and nitronaphthylamines (111, 178, 251, 260). In hydroxycarbonyl compounds, the infrared stretching frequencies of both hydroxyl and carbonyl groups are lowered if they participate in internal hydrogen bonding. Depending on the strength of interaction, the hydroxyl frequency drops from the normal value for free hydroxyl (3600 cm^{-1}) to quite close to the C–H absorption region (2900 cm^{-1}). For instance, in *peri*-hydroxyindanones, ν_{OH} occurs around 3370 cm^{-1}, while, in hydroxytetralones and hydroxybenzocycloheptenones, the much stronger chelation pushes ν_{OH} into the C–H absorption region (193). As judged from these results, internal hydrogen bonding in indanones appears to be weaker than in the higher homologs. This is suggested to be a consequence of the larger distance between the hydrogen-bonding substituents in the indanones compared to their homologs. Essentially similar conclusions emerge from a considera-

tion of the carbonyl absorption frequencies in these compounds.

Thomson (541) has recorded the infrared spectra of some naphthalenediones such as CCLXXV and CCLXXVI and found that introduction of a hydroxyl group *peri* to the carbonyl caused low-frequency carbonyl absorption. Furthermore, the *peri*-hydroxy derivatives do not show free hydroxyl absorption.



CCLXXV

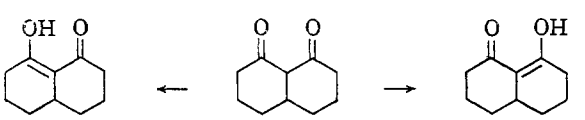


CCLXXVI

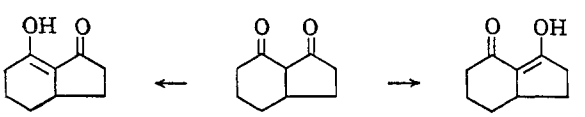
	CCLXXV	CCLXXVI
$\nu_{C=O}$ (cm^{-1})	R = H, 1673	1660
	R = OH, 1677	1667
	1628	1643

In methoxynaphthols, the *peri* isomers have the hydroxyl absorption in the range 3361–3440 cm^{-1}, while the non-*peri* isomers show strong absorption in the normal range of 3603–3609 cm^{-1} (334). Hoyer (282) determined the hydroxyl frequencies in 1,8-dihydroxynaphthalene and 1,8-methoxynaphthol in both carbon tetrachloride and carbon disulfide. In the former compound, both free and hydrogen-bonded hydroxyl frequencies are evident, while in 1,8-methoxynaphthol the observed data indicate only hydrogen-bonded hydroxyl. Despite the extensiveness of the hydrogen bonding, the bond in these compounds is weak, as manifested by the relatively small shift ($\Delta\nu$ = ~0.1 μ) of the OH frequency.

In appropriate cases, hydrogen bonding between *peri* substituents has been the driving force in establishing the equilibrium involving the keto and enol forms of hydroxy ketones. Thus in the case of 1,8-naphthalenedione and hexahydroindan-1,7-dione, the enols would appear to be favored over the keto forms due to stabilization achieved through internal hydrogen bonding in the former. This indeed is what is suggested



CCLXXVII



CCLXXVIII

by infrared spectral data (319a). CCLXXVII shows a broad and strong absorption at 6.22 μ (due to hydrogen bonded carbonyl and conjugated olefin), while in CCLXXVIII the band is less pronounced at 6.15 μ (weaker hydrogen bonding). It is of further interest to note that a supercooled sample of the indandione shows absorption at 5.7–5.8 μ, suggesting free carbonyl.

A comparison of the intensities of the hydroxylic protons at 16.37 ppm in the nmr spectra of these derivatives also indicates that while CCLXXVII is completely enolized in chloroform solution at room temperature, the indan analog is only 87% enolized under the same conditions (319b). This difference is believed to arise from a less favorable O–H · · · O distance in the indandione, precluding effective hydrogen bonding. The complete equivalence of the tautomeric structures for CCLXXVII (as contrasted to those for CCLXXVIII) perhaps drives the keto–enol equilibrium in the former far to the enol side.

Luther and Gunzler (392) have examined the asymmetric and symmetric frequencies of nitro and hydroxyl groups in nitronaphthols. On the basis of their data, they conclude that intramolecular hydrogen bonding is strongest in 1-nitro-2-naphthol and weakest in 8-nitro-1-naphthol. As indicated earlier, the chelate ring in *peri*-nitronaphthol would be again seven-membered.

Diverse opinions have been expressed regarding the hydrogen bonding in nitronaphthylamines. Hathway and Flett (260) studied the N–H and NO_2 vibration frequencies in several of these amines in carbon tetrachloride solution (0.1%) and found significant deviation of both frequencies in *o*-nitroamines (1,2, 2,1, and 2,3) but not in the *peri*-amine (1,8), presumably indicating lack of intramolecular hydrogen bonding in the latter. They (260) attribute this behavior of the *peri*-amine to lack of conjugation between the *peri* substituents. Perhaps both steric and electronic effects are equally important prerequisites for intramolecular hydrogen bonding.

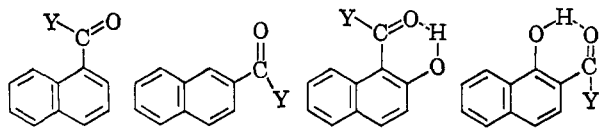
Bryson and Werner (111) have made a more elaborate study of this problem. They measured the asymmetric (ν_{as}) and symmetric (ν_s) N–H vibrations of nitronaphthylamines in carbon tetrachloride and pyridine solutions. From these values, the N–H stretching force constants for these amines can be calculated for each of the two solvents using the equation

$$k = 2.76 \times 10^{-5}(\nu_{as}^2 + \nu_s^2)$$

In pyridine solution there can occur solute–solvent hydrogen bonding leading to a decrease of N–H stretching force constant compared to that in carbon tetrachloride. This decrease in force constant is in the range 0.50–0.66 for non-*ortho* and non-*peri* nitroamines for which Δk values are relatively smaller (0.24 for 1-nitro-2-amine, 0.34 for 2-nitro-1-amine, 0.38 for 3-nitro-2-amine, and 0.31 for 8-nitro-1-amine). This observation may be rationalized as follows: in the former class of amines, both amino hydrogens interact with the solvent while in the *ortho* and *peri* derivatives, one of the amino hydrogens is engaged in hydrogen bonding and hence less influenced by the solvent (data on a compound like 1,3-dinitro-2-aminonaphthalene where both the amino hydrogens would be involved in internal

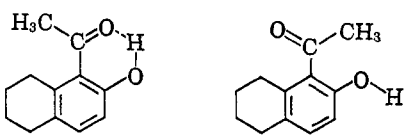
hydrogen bonding should be interesting). Bryson and Werner (111) believe that 8-nitro-1-naphthylamine is hydrogen-bonded. They also suggest that 1-nitro-2-naphthylamine (Δk = 0.24) is more strongly hydrogen-bonded than 2-nitro-1-naphthylamine (Δk = 0.34) as a result of *peri* hindrance to solvation at the 1-amino group in the latter derivative. Dyall and Hambly (178) and Hambly and O'Grady (251) hold the opposite view concerning hydrogen bonding in 1,2 and 2,1 nitroamines, again from infrared measurements. Intramolecular hydrogen bonding in 1,8-naphthalenediamine is also found to be weak, contrary to what one would expect from predictions based on models (251).

peri-Hydrogen is also shown to cause "steric facilitation of chelation" in certain 1,2-disubstituted naphthalenes (286–288). For example, in compounds such as CCLXXIX and CCLXXX, the introduction of an *o*-hydroxyl group causes a lowering of the carbonyl



CCLXXIX CCLXXX CCLXXXI CCLXXXII

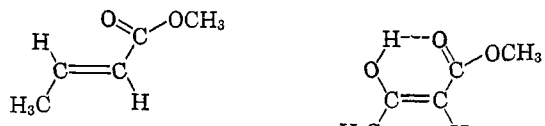
frequency. The magnitude of $\Delta\nu_{C=O}$ may be considered to reflect the strength of the hydrogen bond in these compounds. Thus in passing from CCLXXIX (Y = H, CH_3, or OCH_3) to CCLXXXI the average $\Delta\nu_{C=O}$ is 59 cm^{-1}. The corresponding figure for CCLXXX → CCLXXXII is only 54 cm^{-1}. This is attributed to a buttressing of the 1-carbonyl group in CCLXXXI by *peri*-hydrogen leading to a stronger hydrogen bond; this effect is operative in CCLXXXII also but to a lesser extent, since in the former cases the bulkier –C(Y)=O suffers buttressing, and in the latter only the hydroxyl group is buttressed (286, 288). Similar findings have been made on *ortho*-substituted 5,6,7,8-tetrahydro-1- and -2-naphthols (288). From infrared studies, 5,6,7,8-tetrahydro-1-acetyl-2-naphthol



CCLXXXIII CCLXXXIV

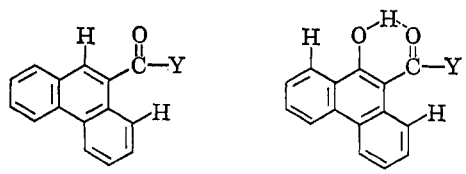
is said to exist mostly in the chelated structure CCLXXXIII (288). However, from ultraviolet absorption data and a study of models, structure CCLXXXIV is suggested for this molecule (457). The large $\Delta\nu_{C=O}$ (54 cm^{-1}) observed for this molecule favors the former structure which provides for effective hydrogen bonding. It would therefore appear that the stabilization gained by internal hydrogen bonding in CCLXXXIII should compensate for the unfavorable steric interactions that would occur in this arrangement. Infrared data indicate both the chelated and nonchelated structures to be present in equilibrium, with the former predominating (*e.g.*, in 5,6,7,8-tetrahydro-1-acetyl-2-naphthol, there occurs strong absorption at 1631 cm^{-1} and a weak absorption at 1685 cm^{-1}; in methyl 5,6,7,8-tetrahydro-2-hydroxy-1-naphthoate, absorption occurs at 1665 and 1733 cm^{-1}).

The concept of steric facilitation of chelation receives further support from studies on some phenanthrene derivatives. In *trans*-methyl crotonate (CCLXXXV), carbonyl absorption occurs at 1726 cm^{-1}. This is pushed down to 1655 cm^{-1} in the



CCLXXXV CCLXXXVI

enolic form of methyl acetoacetate (CCLXXXVI) ($\Delta\nu_{C=O}$ 71 cm^{-1}). For the sterically related pair of phenanthrene derivatives (CCLXXXVII and CCLXXXVIII, Y = OCH_3), $\Delta\nu_{C=O}$ is even higher (75 cm^{-1}). This is again attributed to a buttressing effect of *peri*-



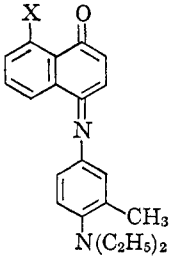
CCLXXXVII CCLXXXVIII

hydrogen. It is of interest to note the higher $\Delta\nu_{C=O}$ in the phenanthrene derivatives over the open-chain systems in spite of a larger bond localization in the latter. Consistent with the above interpretation, $\Delta\nu_{C=O}$ is higher when Y = OCH_3 or CH_3 (75 cm^{-1}) than when Y = H (61 cm^{-1}), the *peri* effect being more with acetyl or methoxycarbonyl than with the formyl group.

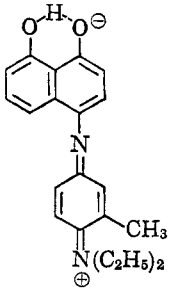
A few illustrations from nmr investigations of *peri*-hydrogen bonding are also available. Brown, Lovie, and Thomson (100) observed the hydroxylic proton signal (in deuteriochloroform solution) for 1-naphthol at τ 4.85. In *ortho*-chelated derivatives such as 2-methoxy-1-naphthol or 1,8-dimethoxy-6-methyl-2-naphthol, the phenolic proton signal is at τ ~4.0. In *peri*-chelated compounds, this resonance absorption is shifted to τ ~0.8, indicating strong hydrogen bonding. These authors have also noted a similar trend with their infrared absorption. The hydroxyl frequency in *o*-methoxynaphthols is observed around 3540 cm^{-1}, while in *peri*-methoxynaphthols the absorption is at 3400 cm^{-1}. Scheiffelle and Shirley (508) have observed the hydroxylic proton signal for juglone at τ −1.86, again suggesting strong intramolecular hydrogen bonding. Similar shifts to lower fields are also observed in the case of 7-hydroxy-1-indanone (τ 1.10) and 8-hydroxy-1-tetralone (τ −2.11) (398).

Dudek (174) has determined the hydroxylic proton resonance in 2-acetyl-1-naphthol and 1-acetyl-2-naphthol. The chemical shift in 1-acetyl-2-naphthol is 13.34 ppm and that in 2-acetyl-1-naphthol is 13.92 ppm. The difference (0.58 ppm) in chemical shift between these compounds is attributed to a relatively stronger hydrogen bonding in the 2-acetyl derivative, though one should also bear in mind the possible variation in chemical shifts arising from ring current anisotropic effect in view of the different orientations of the hydroxyl group (~0.1 ppm). *peri*-Hydrogen sterically hinders internal hydrogen bonding in 1-acetyl-2-naphthol (by twisting the 1-acetyl group out-of-plane) but promotes it in 2-acetyl-1-naphthol (by locking the 1-hydroxyl in the *trans* position). The *trans* conformational preference of the 1-hydroxyl group in 1-naphthol has already been pointed out (484).

Instances (380, 391) where intramolecular hydrogen bonding in *peri*-naphthalene derivatives have been studied by ultraviolet spectral methods are also known. In the group of indoaniline dyes (CCLXXXIX) derived by the oxidative condensation of α-naphthol with 4-amino-2-methyl-N,N-diethylaniline, the absorption maximum occurs at 582 mμ when X = H. When X =



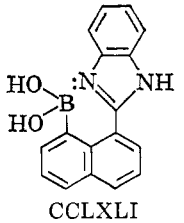
CCLXXXIX



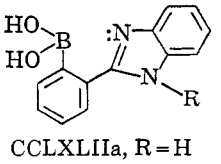
CCLXL

OH, NH_2, or NHR, the absorption is bathochromically displaced to 602–629 mμ. No such shifts are observed with the same substituents at non-*peri* positions. This is presumably due to stabilization of polar structures such as CCLXL which could be visualized for the *peri*-hydroxy (and similar) derivatives (391).

Another illustration of the application of ultraviolet spectroscopy is a somewhat related study on 2-(8-borono-1-naphthyl)benzimidazole (CCLXLI) (380). Changes in the pH of the medium are found to affect



CCLXLI



CCLXLIIa, R = H
b, R = CH_3

profoundly the spectral behavior of CCLXLII but not that of the *peri*-naphthyl derivative. This fact suggests that in the latter, there might be some electronic interaction between boron and nitrogen due to their being in much closer proximity than in the benzene analog. One should, however, note that in the naphthyl derivative, the formation of a coordinate link between boron and nitrogen would lead to a more favored six-membered ring, while in the phenyl derivative, only a five-membered ring could result.

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