matter of convenience. No difficulty was encountered from traces of carbon tetrachloride swept into the alkali trap during chlorination.

Iodine Chloride Titrations.—The limitations of the iodine chloride titration have been discussed. The method of Kemp and Mueller[16] was applied successfully without modifications to polyisoprene, rubber and gutta percha. However, with chlorinated polymers the procedure had to be modified to insure complete iodine chloride addition. The reason for this is two-fold: (1) the reaction is considerably slower for the chlorinated polymers, and (2) the low solubility of some of the chlorinated polymers further retards iodine chloride addition and leads to erratic results, as the titration must be carried out with a gel containing sample. These difficulties were largely overcome by allowing additional time for the iodine chloride addition to take place.

Summary

The extent of additive and substitutive chlorination was determined for emulsion polyisoprene, Hevea and Gutta Percha chlorinated to different chlorine contents in the dark and in a nitrogen atmosphere.

The maximum amount of additive chlorine that can be introduced into the polymer is 1.21 atoms of chlorine per isoprene unit for synthetic emulsion polyisoprene, 1.14 for Hevea. The chlorination involves a cyclization reaction by pairs, leading to isolation of reactive units. The loss in unsaturation due to cyclization has been calculated statistically by the method of Flory and Wall and has been shown to be consistent with the total amount of additive chlorine in the fully chlorinated product.

The cyclization takes place in the early stages of the chlorination simultaneously with the initial substitution. The theoretical limit of cyclization calculated statistically is 86.5% of all isoprene units cyclized for natural rubber and 72% for polyisoprene containing 10% vinyl side chains.

Iodine chloride titration gives fair results for samples of low chlorine content but is not applicable to polymers containing much more than 35% Cl. Knowing the degree of cyclization, the unsaturation can, however, be calculated for any polymer from the extent of additive reaction.

Substitutive chlorination is catalyzed by oxygen and peroxide, additive chlorination by ultraviolet light. Cyclization is partially prevented by the increase in additive reaction. Under the combined effect of peroxides and ultraviolet radiation chlorination can be carried to very high degrees.

BARTLESVILLE, OKLAHOMA RECEIVED APRIL 21, 1949

---

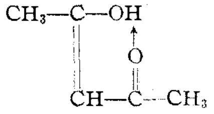
[16] A. R. Kemp and G. S. Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

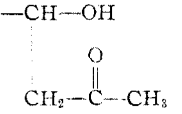
The Determination of Bond Fixation in Cyclic Systems. I. Naphthalene

BY I. MOYER HUNSBERGER[1]

A comparison of the infrared spectra of the enolic form of acetylacetone (I) (containing OH conjugated with C=O) with the corresponding saturated compound (II) (containing OH not conjugated with C=O) has demonstrated the absence of chelation in the latter.[2]



I



II

Although in some cases chelation apparently is possible without conjugation between the chelated groups, there seems no doubt that the most strongly chelated compounds owe their character to a high degree of conjugation. These "conjugated chelate" systems recently have been adequately discussed.[3]

If chelated substituents are present on an aromatic ring, the strength of chelation obviously should depend on the degree of "doublebondedness" of the bond joining the ring carbon atoms holding the substituents. Thus, Calvin and Melchior[4] recently found that metallic chelates derived from 3-hydroxy-2-naphthaldehyde were less stable than those from its 1,2- or 2,1- isomers. They attributed this behavior to the greater double bond character of the nuclear C_1–C_2 bond as compared to the C_2–C_3 bond. Melchior[5] also has explained differences in the ultraviolet spectra of these aldehydes on the same basis. Baker[6] earlier had pointed out that any difference in the strength of chelation between isomeric 1,2- (or 2,1-) and 2,3- disubstituted naphthalenes could be explained on the basis of a more or less fixed nuclear double bond structure. However, from a comparison of the wet melting points and critical solution temperatures of the 1,2-, 2,1- and 3,2- hydroxyacetonaphthones Baker[6] concluded that all isomers apparently were almost equally strongly chelated. As a result, an obviously attractive physical method for detecting bond fixation by measuring the strength of chelation in appropriate *o*- disubstituted isomers of a given ring system failed to materialize.

Other physical methods which have been used

---

[1] Department of Chemistry, Antioch College, Yellow Springs, Ohio.

[2] Freymann and Heilmann, *Compt. rend.*, **219**, 415 (1944).

[3] (a) Rasmussen, Tunnicliff and Brattain, THIS JOURNAL, **71**, 1068 (1949); (b) Rasmussen and Brattain, *ibid.*, **71**, 1073 (1949).

[4] Calvin and Melchior, *ibid.*, **70**, 3273 (1948).

[5] Melchior, *ibid.*, **71**, 3647 (1949).

[6] Baker and Carruthers, *J. Chem. Soc.*, 479 (1937).

to detect bond fixation in naphthalene include the comparison of acidity of *o*-hydroxynaphthaldehydes[7a] and *o*-chloronaphthoic acids[7b] and the measurement of bond distances by X-ray methods.[7c] Unfortunately, these methods have not given entirely concordant results.

Cryoscopic Work.—The present investigation was initiated in the belief that a more sensitive physical method for measuring the strength of an intramolecular hydrogen bond might reveal the distinctions Baker and Carruthers[6] failed to demonstrate conclusively. Accordingly, the molecular weights of the same three hydroxyacetonaphthones were determined cryoscopically in naphthalene solution at a series of concentrations up to about 0.7 molal. It was hoped that the least strongly chelated isomer would show at least a slight degree of association in the more concentrated solutions.

Many preliminary attempts to use the apparatus originally described by Auwers[8] and extensively used recently with evidently little or no modification by Hunter[9] convinced the author that the errors caused by sublimation of the solvent naphthalene cannot be disregarded in accurate work. Long ago Mathews[10] pointed out this error, but his apparatus, designed to eliminate it, requires quite complicated equipment. The experimental procedure also apparently is rather time-consuming. In the present work a cryoscopic apparatus was constructed from readily available materials which permitted high accuracy without long and involved experimental manipulation (*cf.* experimental part).

The results of molecular weight determinations on the three hydroxyacetonaphthones along with the corresponding hydroxynaphthaldehydes and methyl hydroxynaphthoates are graphically presented in Fig. 1. For comparison, data are included which were calculated from Auwers' molecular weight determinations[8] on the methyl hydroxynaphthoates in naphthalene solution. Auwers' data for the 2-hydroxy-1-ester are not plotted, as his sample (m. p. 69°) admittedly was highly impure.

It is immediately apparent that not even a slight degree of association could be detected in any compound examined. All were essentially monomeric throughout the concentration range studied. These results merely show that the cryoscopic behavior of chelated 1,2-, 2,1- and 3,2-disubstituted naphthalenes corresponds to that of analogous benzene derivatives. Furthermore, wet melting point determinations on methyl 3-hydroxy- and 1-hydroxy-2-naphthoate also were unable to show any distinct difference in degree of chelation in these compounds (*cf.* experimental part).

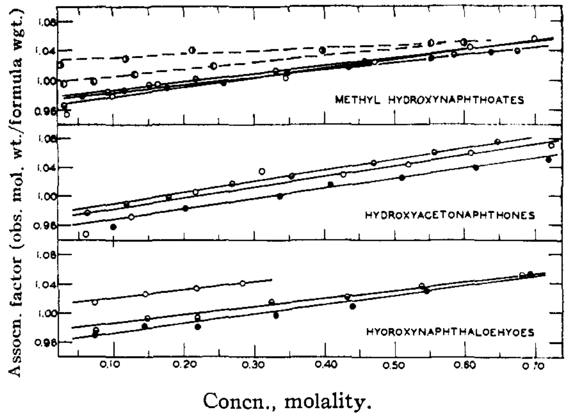


Fig. 1.—Cryoscopic data: —○— 1-hydroxy-2-ester, ketone and aldehyde; —●— 2-hydroxy-1-ester, ketone and aldehyde; —◓— 3-hydroxy-2-ester, ketone and aldehyde; ---◐--- Auwers' data[8] for 1-hydroxy-2-ester; ---◑--- Auwers' data[8] for 3-hydroxy-2-ester.

In view of the results presented below the failure of this cryoscopic attack to show the expected differences among isomers presumably is explained merely by assuming that relatively weak chelation is sufficient to enable monomeric character to be retained even in concentrated solutions, where some association might otherwise be expected.

Infrared Work.—Although early workers[11] concluded that chelated compounds could be distinguished by their lack of OH absorption in the region of the first overtone when examined in dilute carbon tetrachloride solution, it soon became evident the OH bands usually appear in the region of the fundamental absorption but either at a position greatly displaced to longer wave lengths or merged with the CH absorption.[12] That the amount of this displacement roughly parallels the energy of the hydrogen bond is indicated by the work of several authors.[13]

There also seems to be ample evidence that the formation of a hydrogen bond is similarly manifested in the shift of the carbonyl absorption from its normal position to distinctly longer wave lengths.[3,14] From certain of these works[3,14e,f] it seems evident that the magnitude of this shift, though much less than the corresponding OH shift, also parallels the energy of the hydrogen bond. Furthermore, the displaced C=O band usually is much sharper, relatively less displaced

---

(7) (a) Arnold and Sprung, THIS JOURNAL, **60**, 1163 (1938); (b) Bergmann and Hirshberg, *J. Chem. Soc.*, 331 (1936); (c) Robertson, *Proc. Roy. Soc.* (*London*), **A142**, 674 (1933).

(8) Auwers, *Z. physik. Chem.*, **18**, 595 (1895).

(9) Hunter, *et al.*, *J. Chem. Soc.*, 874 (1948), and earlier papers.

(10) Mathews, THIS JOURNAL, **39**, 1125 (1917).

(11) Hilbert, Wulf, Hendricks and Liddel, *ibid.*, **58**, 548 (1936); Errera and Mollet, *J. phys. radium*, [7] **6**, 281 (1935).

(12) Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 84, 501 (1937); Errera and Sack, *Trans. Faraday Soc.*, **34**, 728 (1938).

(13) Badger and Bauer, *J. Chem. Phys.*, **5**, 839 (1937); Badger, *ibid.*, **8**, 288 (1940); Fox and Martin, *Proc. Roy. Soc.* (*London*), **A162**, 419 (1937); Gordy, *J. Chem. Phys.*, **7**, 167 (1939); Gordy and Stanford, *ibid.*, **8**, 170 (1940); Davies, *Trans. Faraday Soc.*, **36**, 1114 (1940). However, see Sutherland, *ibid.*, **36**, 889 (1940); *J. Chem. Phys.*, **8**, 161 (1940).

(14) (a) Barnes, *Rev. Sci. Instruments*, **7**, 265 (1936); (b) Williams and Gordy, THIS JOURNAL, **59**, 817 (1937); (c) Davies and Sutherland, *J. Chem. Phys.*, **6**, 755 (1938); (d) Gordy, THIS JOURNAL, **60**, 605 (1938); (e) Gordy, *J. Chem. Phys.*, **8**, 516 (1940); (f) Flett, *J. Chem. Soc.*, 1441 (1948).

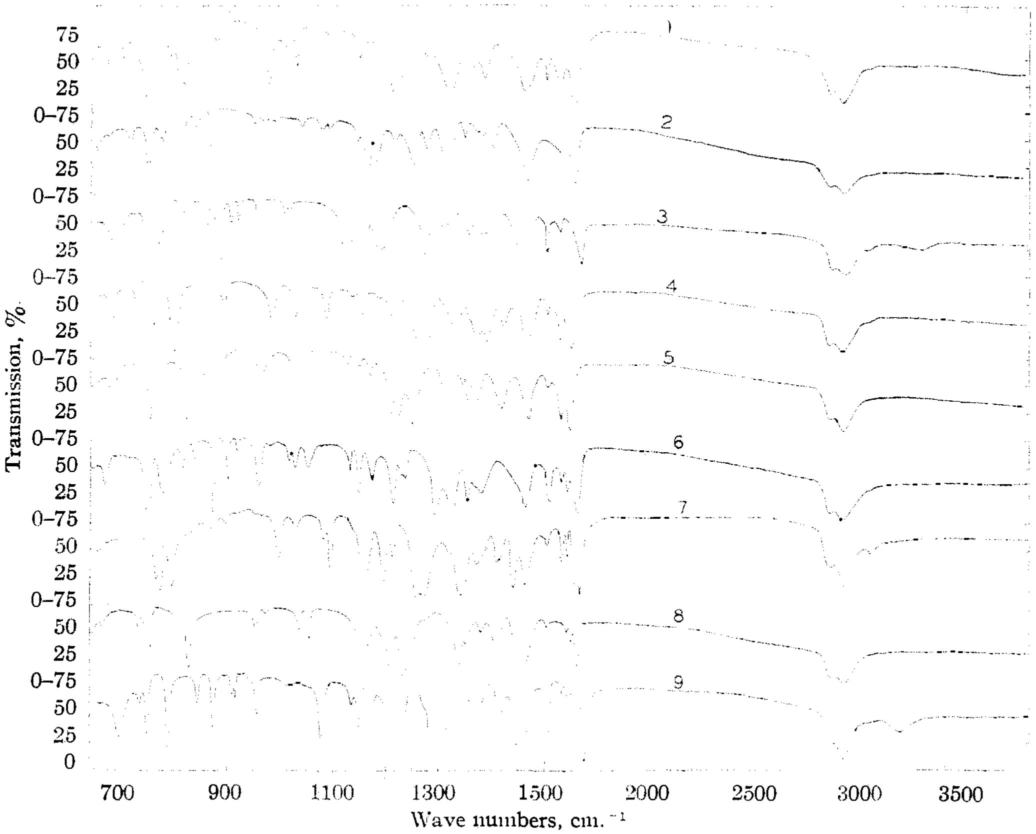


Fig. 2.—Infrared spectra of Nujol mulls: 1, 1-hydroxy-2-naphthaldehyde; 2, 2-hydroxy-1-naphthaldehyde; 3, 3-hydroxy-2-naphthaldehyde; 4, 1-hydroxy-2-acetonaphthone; 5, 2-hydroxy-1-acetonaphthone; 6, 3-hydroxy-2-acetonaphthone; 7, methyl 1-hydroxy-2-naphthoate; 8, methyl 2-hydroxy-1-naphthoate; 9, methyl 3-hydroxy-2-naphthoate.

and therefore easier to identify and locate accurately.

By making use of infrared spectra and interpreting them in terms of the above considerations a clear demonstration was obtained that chelation in 1,2- and 2,1-disubstituted naphthalenes is of very nearly identical strength and considerably stronger than in the isomeric 2,3-derivatives. The spectra of highly purified samples of the three hydroxyacetonaphthones, hydroxynaphthaldehydes, and methyl hydroxynaphthoates were determined as mulls in Nujol (Fig. 2) and as 0.02 molal solutions in carbon tetrachloride (Fig. 3, aldehydes; Fig. 4, ketones; Fig. 5, esters), the thickness of the sample layer being kept constant at 1.5 mm. except for a very few of the solution spectra in which a thickness of 0.16 mm. permitted better resolution of the carbonyl absorption. In this way, all compounds were examined under identical conditions. The C=O band positions for all compounds as mulls in Nujol and in solution in carbon tetrachloride are collected in Table I.

An examination of the spectra obtained in Nujol (Table I and Fig. 2) reveals that the 1,2- and 2,1-isomers in all three series are so strongly bonded that no distinct OH band is recognizable.

TABLE I

CARBONYL BANDS

Compound	C=O Bands (cm.$^{-1}$) In Nujol	In 0.02 molal CCl_4	ΔC=O (cm.$^{-1}$)
α-Naphthaldehyde		1700	
β-Naphthaldehyde		1702	
1-Hydroxy-2-naphthaldehyde		1651[a]	50[a]
	ca. 1632	1637	64
2-Hydroxy-1-naphthaldehyde		1649[a]	52[a]
	1637	1638	63
3-Hydroxy-2-naphthalehyde	1670	1670	31
α-Acetonaphthone		1685	
β-Acetonaphthone		1685	
1-Hydroxy-2-acetonaphthone		1625[a]	60[a]
	1625	1630	55
2-Hydroxy-1-acetonaphthone		1625[a]	60[a]
	1620	1629	56
3-Hydroxy-2-acetonaphthone	1651	1657	28
Methyl α-naphthoate		1724	
Methyl β-naphthoate		1726	
Methyl 1-hydroxy-2-naphthoate	1665	1668	57
Methyl 2-hydroxy-1-naphthoate	1653	1657	68
Methyl 3-hydroxy-2-naphthoate	1685	1691	34

[a] Thickness of the sample layer, 0.16 mm.

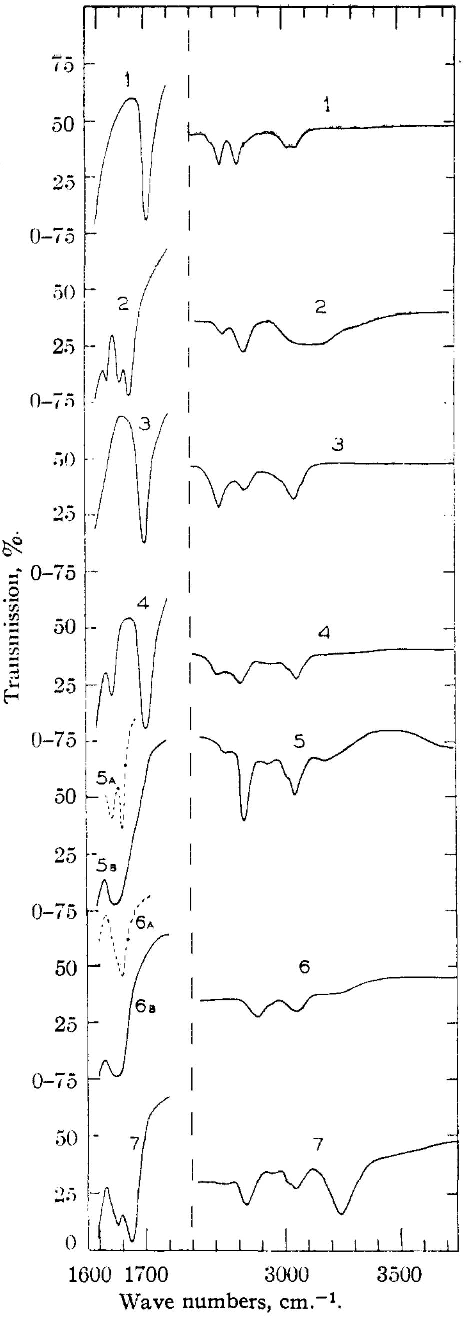


Fig. 3.—Infrared spectra of aldehydes in 0.02 molal solutions in carbon tetrachloride: 1, benzaldehyde; 2, salicylaldehyde; 3, α-naphthaldehyde; 4, β-naphthaldehyde; 5, 1-hydroxy-2-naphthaldehyde; 6, 2-hydroxy-1-naphthaldehyde: 7, 3-hydroxy-2-naphthaldehyde; A, 0.16-mm. layer.

Instead, only slight "dips" are evident on the short wave length side of the CH absorption. While the same consideration applies to 3-hydroxy-2-acetonaphthone (Curve 6, Fig. 2), the corresponding aldehyde (Curve 3, Fig. 2) and ester (Curve 9, Fig. 2) show definite OH bands (Nujol) at 3295 cm.$^{-1}$ and 3184 cm.$^{-1}$, respectively.

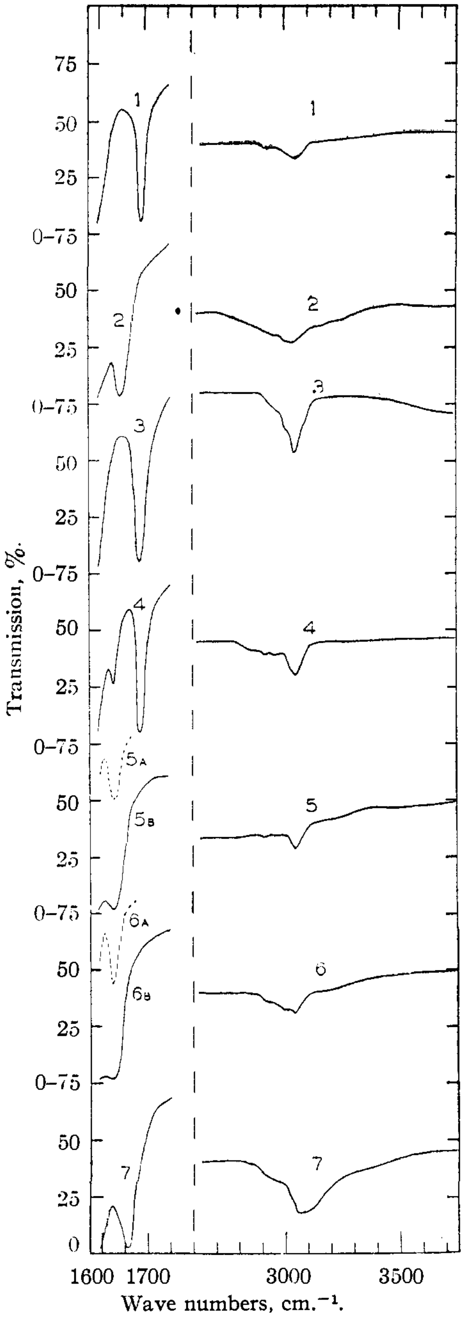


Fig. 4.—Infrared spectra of ketones in 0.02 molal solutions in carbon tetrachloride: 1, acetophenone; 2. *o*-hydroxyacetophenone; 3, α-acetonaphthone; 4, β-acetonaphthone; 5, 1-hydroxy-2-acetonaphthone: 6. 2-hydroxy-1-acetonaphthone; 7, 3-hydroxy-2-acetonaphthone; A, 0.16-mm. layer.

These data are considered good qualitative evidence that all compounds examined exhibit strong intramolecular hydrogen bonds but that the bond in the 3,2-isomer of any series is in general less strong than in the 1,2- or 2,1-isomers of the same series. That 3-hydroxy-2-acetonaphthone is the only 3,2- compound to show no dis-

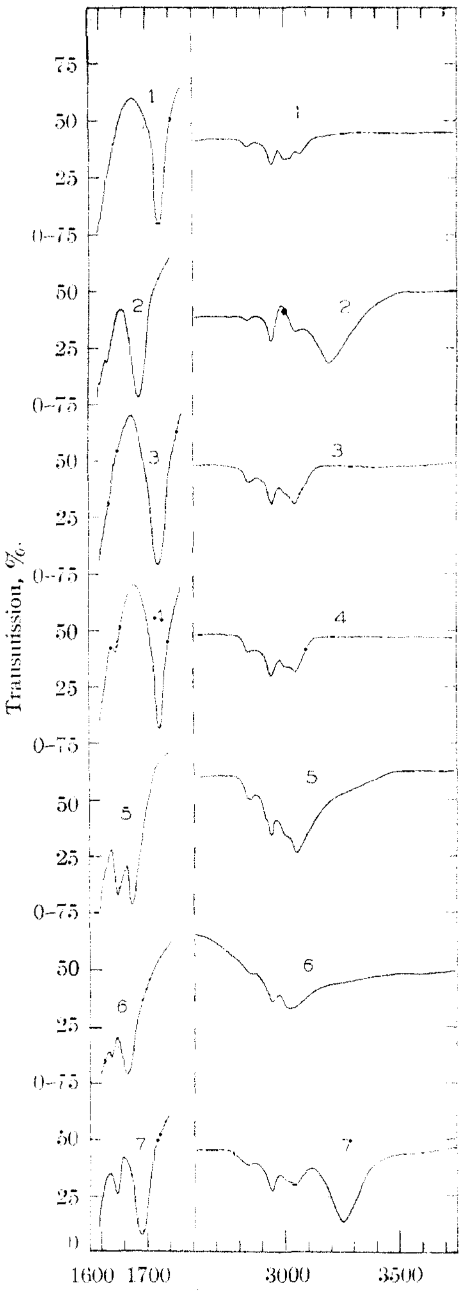


Fig. 5.—Infrared spectra of esters in 0.02 molal solutions in carbon tetrachloride: 1, methyl benzoate; 2, methyl salicylate; 3, methyl α-naphthoate; 4, methyl β-naphthoate; 5, methyl 1-hydroxy-2-naphthoate; 6, methyl 2-hydroxy-1-naphthoate; 7, methyl 3-hydroxy-2-naphthoate.

tinct OH band probably means only that the ketone group forms the strongest hydrogen bond with the OH group. Examination of the positions of carbonyl absorption (Nujol) in Table I makes it immediately apparent that in each series the 1,2- and 2,1-isomers have C═O bands at almost identical positions and rather noticeably displaced toward longer wave lengths, whereas the 3,2-isomers show bands considerably less displaced. These data roughly parallel those concerning OH absorption and indicate the same conclusion. The utility of the spectra of the Nujol mulls is limited by the lack of information concerning the "normal" position of absorption of the functional groups in question (*cf.* below).

More quantitative data were obtained from the solution spectra (Table I and Figs. 3–6). An examination of 0.02 molal solutions of α- and β-naphthol (Curves 2 and 3, Fig. 6), α- and β-acetonaphthone (Curves 3 and 4, Fig. 4), α- and β-naphthaldehyde (Curves 3 and 4, Fig. 3), and methyl α- and β-naphthoate (Curves 3 and 4, Fig. 5) permitted the determination of the "normal" positions of hydroxyl, ketone, aldehyde and ester absorption, respectively, when these groups are attached to the naphthalene nucleus and are undisturbed by other effects. It is reasonable to infer from these spectra that the position of OH and C═O absorption in these monosubstituted compounds is independent of α- or β-substitution. The arithmetic average of the band positions for the α- and β-monosubstituted compounds is taken as the "normal" position of absorption for the functional group in question. In proceeding to the disubstituted compounds, the displacements of the OH band (ΔOH) from its "average" position (3618 cm.$^{-1}$) in α- and β-naphthol and the displacements of the C═O band (ΔC═O) from its "average" position in the corresponding monosubstituted α- and β-carbonyl compounds are taken as semiquantitative measures of the strength of the intramolecular hydrogen bond in the disubstituted compounds. ΔC═O values are collected in Table I. Greater displacements of the "normal" band positions toward longer wave length, *i. e.*, larger values for ΔOH and ΔC═O, are taken as evidence for correspondingly stronger intramolecular hydrogen bonds. The 1,2- and 2,1-compounds again exhibited in general no distinctly recognizable OH bands, since they had apparently shifted to such long wave lengths as to merge almost completely with the CH absorption. Although approximate OH band positions could be located for the 1,2- and 2,1-aldehydes (Curves 5 and 6, Fig. 3) at *ca.* 3178 cm.$^{-1}$ (ΔOH, *ca.* 440 cm.$^{-1}$) and 3240 cm.$^{-1}$ (ΔOH, *ca.* 378 cm.$^{-1}$), respectively, the corresponding ketones (Curves 5 and 6, Fig. 4) and esters (Curves 5 and 6, Fig. 5) showed merely the slightest indication of such a band. However, all three 3,2-isomers showed much more distinct and much less displaced OH bands. Only in the case of 3-hydroxy-2-acetonaphthone (Curve 7, Fig. 4) could the position of the OH band (estimated at *ca.* 3090 cm.$^{-1}$) not be located accurately. The OH bands in the 3,2-aldehyde (Curve 7, Fig. 3) and -ester (Curve 7, Fig. 5) could be located unambiguously and accurately at 3249 cm.$^{-1}$ and 3258 cm.$^{-1}$, respectively. Values of ΔOH for the 3,2-aldehyde, ester and ketone thus are 369, 360 and *ca.* 528 cm.$^{-1}$, respectively. The fact that a distinct OH band was shown in each series only by the 3,2-isomer again is taken as qualitative evidence for the weaker intramolecular hydrogen bonding in this isomer.

The undisturbed C=O band in α- and β-acetonaphthone (Curves 3 and 4, Fig. 4) in 0.02 molal solution is located at 1685 cm.$^{-1}$ in each compound. In passing to 1-hydroxy-2-acetonaphthone (Curve 5, Fig. 4) and 2-hydroxy-1-acetonaphthone (Curve 6, Fig. 4) this band was found shifted to 1630 cm.$^{-1}$ and 1629 cm.$^{-1}$, respectively, for a thickness of 1.5 mm., and to 1625 cm.$^{-1}$ in each case for a thickness of 0.16 mm. The corresponding ΔC=O values are 55 cm.$^{-1}$ and 56 cm.$^{-1}$ for the 1.5 mm. layer and 60 cm.$^{-1}$ in each case for the 0.16 mm. layer. On the other hand, the C=O band of 3-hydroxy-2-acetonaphthone (Curve 7, Fig. 4) appeared at 1657 cm.$^{-1}$, thus giving a ΔC=O value of only 28 cm.$^{-1}$ Similar and just as distinct differences were obtained with the corresponding hydroxynaphthaldehydes and methyl hydroxynaphthoates, for which the "average" positions of undisturbed "normal" carbonyl vibrations were 1701 cm.$^{-1}$ and 1725 cm.$^{-1}$, respectively. These data are considered the best evidence for the proposition that in any one series the 1,2- and 2,1-disubstituted naphthalenes exhibit chelation of nearly identical strength which also is considerably stronger than that shown by the isomeric 2,3-compounds.

It appears evident that the only explanation for the observed differences in the strength of chelation in the disubstituted naphthalenes examined appears to lie in the fact that the C_1–C_2 bond of the nucleus has greater double bond character than the C_2–C_3 bond. This in turn facilitates greater conjugation between 1,2- or 2,1-substituents as compared to the 2,3-substituents. Since any extranuclear effect between substituents must necessarily be the same in all three isomers of a given series, the variations in strength of the intramolecular hydrogen bond must be caused by a parallel variation in degree of conjugation.

It might be argued that the known ability of chelated substituents partiallly to fix the double bonds of a resonating structure[15] and thus enhance conjugation would invalidate the conclusions just drawn. However, it must be realized that such "induced" fixation probably would increase the contribution of the structure in question to the resonance of the molecule by no more than about 10%.[16] Furthermore, any such effect would increase the strength of chelation in all three isomers of a given series by the same amount. Hence, it seems safe to apply conclusions from the above data to the unsubstituted ring system.

It is believed that the use of infrared spectra as outlined offers a reliable and convenient physical method for detecting and measuring bond fixation and that the method is capable of rather fine distinctions and of ready application to a variety of ring systems. The naphthalene ring was chosen as a start since the condition of its bonds is known more certainly than that of any other cyclic system.

It should be emphasized that, while classical chemical methods necessarily measure the degree of bond fixation in the activated state during chemical reaction, this new method, like other physical methods, measures the degree of bond fixation in the normal state of the molecule, which undoubtedly is much less than in the activated state. This consideration emphasizes the necessity for sensitivity in any physical method used to detect bond fixation.

The results of the present investigation seem to exclude the possibility that 2,3-disubstituted naphthalenes capable of chelation exhibit a preference for the unsymmetrical Erdmann structure, for it will be shown later that chelation in the 2,3-compounds is less strong than in analogous benzene derivatives. This consideration forces the conclusion that the C_2–C_3 bond in 2,3-disubstituted naphthalenes must exhibit less than 50% double bond character. Bergmann's conclusion[17] that chelated 2,3-disubstituted naphthalenes have an unsymmetrical bond structure was based mainly on the yellow color of certain of these compounds and on the ability of 3-hydroxy-2-acetonaphthone to form metallic complexes. If the unsymmetrical structure (with a double bond between substituents) predominates in such compounds, the diazo coupling of 3-hydroxy-2-naphthoic acid at C_1[18] would be very difficult to explain. Furthermore, the observation[17a] that methyl 3-allyloxy-2-naphthoate rearranges (Claisen) to form methyl 1-allyl-2-hydroxy-3-naphthoate yields no information concerning the status of the double bonds in methyl 3-hydroxy-2-naphthoate (in case this compound should have an unsymmetrical bond arrangement). Calvin and Melchior's work[4,5] also argues against any formula for chelated 2,3-disubstituted naphthalenes which gives the C_2–C_3 bond greater double bond character than the C_1–C_2 bond.

In this connection it must be admitted that no theory thus far devised explains Gilman's seemingly anomalous Dry Ice carbonation of metalated (Li) β-naphthol with the exclusive formation, though in low yield, of 3-hydroxy-2-naphthoic acid.[19] Perhaps an enolic activated complex is unnecessary for this reaction.

If no bond fixation exists in the benzene ring, *i. e.* each bond has 50% double bond character, and if some symmetrical bond fixation of the degree indicated by Pauling[20] exists in naphthalene,

---

[15] (a) Baker, *J. Chem. Soc.*, 1684 (1934); (b) Baker and Lothian, *ibid.*, 628 (1935); 274 (1936).

[16] Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, p. 332.

[17] (a) Bergmann and Berlin, *J. Org. Chem.*, **3**, 246 (1938); (b) Bergmann, "Isomerism and Isomerization of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 17–19.

[18] Kostanecki, *Ber.*, **26**, 2897 (1893).

[19] Gilman, Arntzen and Webb, *J. Org. Chem.*, **10**, 374 (1945).

[20] Ref. 16, p. 142.

the strength of chelation in a given *o*-disubstituted benzene should be almost exactly intermediate between that shown by the analogous 1,2- (or 2,1-) and 3,2-disubstituted naphthalenes.[21]

In order to obtain evidence for this hypothesis the infrared spectra of highly purified samples of phenol (Curve 1, Fig. 6; OH band, 3628 cm.$^{-1}$), acetophenone (Curve 1, Fig. 4; C=O band, 1693 cm.$^{-1}$), *o*-hydroxyacetophenone (Curve 2, Fig. 4; C=O band, 1648 cm.$^{-1}$), benzaldehyde (Curve 1, Fig. 3; C=O band, 1708 cm.$^{-1}$), salicylaldehyde (Curve 2, Fig. 3; C=O band, 1670 cm.$^{-1}$), methyl benzoate (Curve 1, Fig. 5; C=O band, 1730 cm.$^{-1}$) and methyl salicylate (Curve 2, Fig. 5; C=O band, 1683 cm.$^{-1}$) in 0.02 molal solutions in carbon tetrachloride were examined. The greatly shifted OH absorption bands in the disubstituted compounds were either partially or completely merged with the CH absorption, except in the case of methyl salicylate (OH band, 3195 cm.$^{-1}$). However, these OH bands, in general, were displaced further toward longer wave lengths than those of the corresponding 3,2-naphthalenes, thus indicating somewhat stronger chelation in the benzene derivatives.

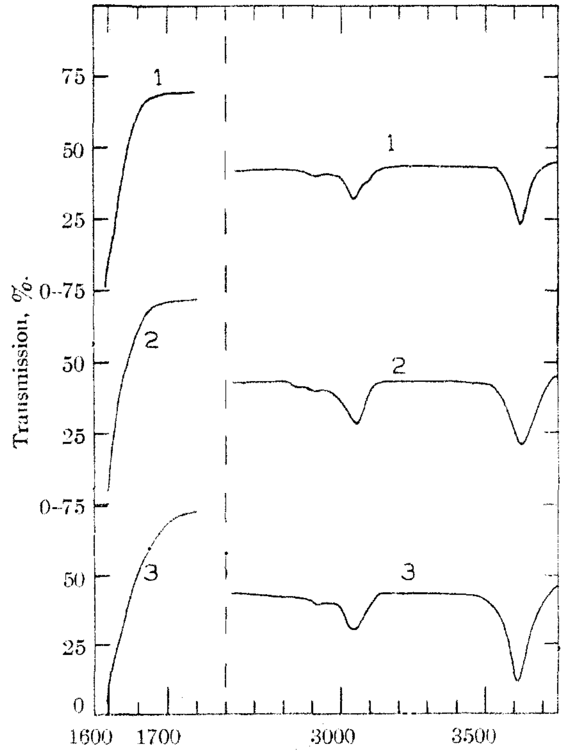


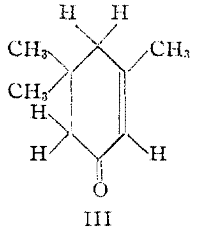
Fig. 6.—Infrared spectra of phenols in 0.02 molal solutions in carbon tetrachloride: 1, phenol; 2, α-naphthol; 3, β-naphthol.

More quantitative evidence resulted from an examination of the region of carbonyl absorption. In proceeding from acetophenone (C=O band, 1693 cm.$^{-1}$) to *o*-hydroxyacetophenone (C=O band, 1648 cm.$^{-1}$), the C=O band was displaced 45 cm.$^{-1}$, which is intermediate between the 28 cm.$^{-1}$ and the 55 or 56 cm.$^{-1}$ shifts caused by proceeding from α- and β-acetonaphthone to 3-hydroxy-2-acetonaphthone and 1,2- or 2,1-hydroxyacetonaphthone, respectively. It is obvious from the listed band positions that analogous results were obtained in the aldehyde and ester series. In each case the above hypothesis apparently was confirmed.

An extension of this argument leads one to predict that any property of an *o*-disubstituted benzene which depends on conjugation between substituents should be intermediate in value between that for the corresponding 1,2- (or 2,1-) and 3,2-naphthalene derivative. The principle of vinylogy[22] shows the acid dissociation constant of an *o*-substituted phenol to be such a property. In agreement with the prediction, both 1-hydroxy-2-naphthaldehyde and 2-hydroxy-1-naphthaldehyde have been found to be considerably stronger acids than salicylaldehyde, which in turn is a stronger acid than 3-hydroxy-2-naphthaldehyde.[7a,23]

An extension of this spectral attack on the problem of bond fixation is in progress.

Bond Fixation and Interpretation of Infrared Spectra.—It has recently been pointed out that the factors influencing the shift in C=O absorption toward longer wave lengths in going from unconjugated to conjugated ketones are not understood.[3a] It would seem reasonable, however, to suppose that the magnitude of this shift should increase with increase in double bond character of the bond in conjugation with the carbonyl group. Hence, it would be expected that in going from an unconjugated ketone (C=O band near 1715 cm.$^{-1}$ [3a]) to acetophenone to α- or β-acetonaphthone the position of the C=O band would move progressively to longer wave lengths. Since acetophenone absorbs at 1693 cm.$^{-1}$ and α- and β-acetonaphthone both absorb at 1685 cm.$^{-1}$, this prediction appears confirmed. Comparison of the C=O band positions of benzaldehyde with α- and β-naphthaldehyde and of methyl benzoate with methyl α- and β-naphthoate shows that the same effect apparently operates in these compounds. Furthermore, such a consideration also apparently explains why isophorone (III) (containing a fixed double bond) shows a C=O band at 1672 cm.$^{-1}$,[3a]



III

---

[21] This reasoning is independent of any alteration in bond fixation caused by the substituents.

[22] Fuson, *Chem. Rev.*, **16**, 1 (1935).

[23] Arnold and Sprung, This Journal, **61**, 2475 (1939).

which is at even higher wave length than that of α- and β-acetonaphthone.

It should be emphasized that any attempt to explain small differences in spectral band positions is fraught with uncertainty, but the preceding correlations appear useful. For such considerations to have maximum validity the spectra should be obtained from use of the same spectrometer under identical conditions on pure samples of the compounds in question. As a result, the author also believes that a detailed comparison of the spectra obtained in this investigation with those obtained for some of the simpler compounds by others would serve no useful purpose. However, an intensive search of the literature failed to reveal any glaring discrepancies.

Experimental[24]

Cryoscopic Apparatus and Determinations.—A 200 × 25 mm. test-tube was used as the f. p. tube. Twelve turns of No. 32 Chromel resistance ribbon (1.6 mm. wide) were fastened ("Sauereisen") on the outside around the upper 9 cm. of this tube. A current sufficient to produce a constant temperature of 75° in the inside upper portion of the tube was passed through this coil during all determinations. This device proved just as effective in preventing condensation of naphthalene vapor but less awkward and more permanent than any of several modifications attempted on the previously used[10] coil of fine wire encircling the thermometer. The leads to the coil were cemented to iron posts mounted on a 5.5-cm. ring of asbestos board cemented ("Sauereisen") around the extreme top of the f. p. tube. This ring also served to suspend the tube in the 5.5 cm. × 30 cm. tubular air jacket which was permanently mounted in the 30 cm. × 30 cm. Pyrex jar used to contain the 50:50 mixture of glycerol and water used as the thermostat liquid. The temperature of this circulating liquid, controlled by a mercury regulator, was always maintained 1.5–2.5° below the f. p. of the melt.

The manually operated stirrer consisted of a straight length of No. 16 Chromel wire which contained two rings 2.5 cm. apart at the bottom to enclose the thermometer bulb. In order to obtain a tight fit through the 12.5 cm. length of 3 mm. Pyrex tubing used as the stirrer jacket, this wire was inserted through a 15 cm. length of 2 mm. tubing, the lower end of which was cemented ("Sauereisen") to the stirrer wire at a point 10 cm. from the bottom. By allowing 3 cm. of the jacket to extend below the rubber stopper used to mount the stirrer and thermometer, the "Sauereisen" seal served as the upper "stop" for the stirrer stroke. This simple device withstood the vigorous stirring required near the f. p. much more satisfactorily than the conventional glass rod. Furthermore, by lubricating the stirrer jacket with a liberal coat of Silicone vacuum grease a seal was obtained which almost entirely prevented the escape of naphthalene vapor. This was found much more effective than a variety of other devices tried in the search for a vapor-tight seal. Even in Mathews' refined equipment[10] it would seem that some vapor must necessarily escape through the stirrer jacket.

Instead of the usual Beckmann, a specially constructed thermometer (8 mm. diameter) calibrated to 0.01° and reading permanently between 75° and 81° was purchased from Rascher and Betzold, Chicago, Ill. This thermometer could easily be read to 0.001° and was found eminently satisfactory. However, best results were obtained if, prior to a determination, the thermometer was permitted to stand overnight in 22–23 g. of solvent naphthalene held 1–1.5° above its f. p. This procedure entirely eliminated the several hours otherwise required by the thermometer to adjust itself so as to give dependable readings.

The solvent naphthalene was the twice recrystallized commercial product. An additional sublimation at high vacuum followed by another recrystallization produced no better product. Over a series of several hundred determinations performed over a period of eight months the m. p. of the naphthalene varied from a low of 79.822° to a high of 80.059°.

The contents of the freezing point tube were quickly melted by inserting it into an air jacket (15 cm. × 5 cm. Pyrex tube) permanently heated to about 90° by a coil of resistance wire. The temperature of the melt was never raised more than 1.5–2° above its f. p. Solute was added as small pellets.

During the f. p. determinations supercooling was held to about 0.1° or less by very vigorous stirring. Each molecular weight was calculated from the average of at least two freezing point determinations differing usually by no more than 0.002–0.003°. In a few of the most concentrated solutions the concordance was no better than 0.005–0.008°. Seeding of the melt was accomplished by introducing a crystal of naphthalene through a hole in the rubber stopper which otherwise was plugged with an easily removable tapered glass rod.

Infrared Work.—All spectra were determined using a Model 12B Perkin–Elmer Spectrometer with rock salt optics. The thickness of the sample layer was held constant at 1.5 mm. except for the few cases noted in Table I and Figs. 3 and 4, when a 0.16 mm. thickness permitted better resolution of the bands. Redistilled Baker and Adamson Reagent carbon tetrachloride was used in making all the solutions. Both solute and solvent were accurately weighed. Easily oxidized samples were examined within thirty minutes after completion of the final purification.

Preparation of Materials.—**1-Hydroxy-2-acetonaphthone** was prepared according to Witt and Braun[25] and recrystallized four times from ethanol to yield pale yellow crystals with a faint greenish tinge, m. p. 97.2–98.8° (cor.).[26] **2-Hydroxy-1-acetonaphthone** was prepared according to Fries.[27] The steam distilled product, obtained in 48% yield, crystallized from hexane as practically colorless crystals, m. p. 63–64°; lit. m. p. 64°.[6,27]

3-Hydroxy-2-acetonaphthone.—This compound was prepared from 3-methoxy-2-naphthoyl chloride *via* the intermediate 3-methoxy-2-acetonaphthone.[6,28] By using dimethylcadmium instead of methylzinc iodide the preparation of the methoxyketone was greatly improved:

Following Cason,[29] 9.15 g. (0.05 mole) of anhydrous cadmium chloride was added over a five-minute period (nitrogen atmosphere) to 26 ml. of a cold stirred 4 *M* solution of methylmagnesium bromide in absolute ether (Arapahoe). The mixture was refluxed until a negative test for Grignard was obtained (thirty minutes). The ether was removed by distillation and replaced by 60 ml. of dry benzene. At 10–18° a solution of 10.8 g. (0.0489 mole) of 3-methoxy-2-naphthoyl chloride in 45 ml. of dry benzene was gradually added over fifteen minutes. When the exothermic reaction ceased, the mixture was allowed to warm to room temperature, stirred for forty minutes at this temperature and then for ninety minutes at 45°. The cooled mixture was carefully treated with ice and water, followed by enough dilute sulfuric acid to dissolve the white precipitate. The layers were separated and the aqueous layer re-extracted twice with benzene. The combined, dry benzene extracts were distilled. After all benzene was removed, the residue yielded 8.8 g. (90%) of

---

(24) All boiling points and melting points are uncorrected unless specified otherwise.

(25) Witt and Braun, *Ber.*, **47**, 3216 (1914).

(26) Witt and Braun (ref. 25) report m. p. 101-103° changing to 98-99° on further crystallization. Torrey and Brewster [THIS JOURNAL, **35**, 426 (1913)] mention a similar phenomenon. Other m. p.'s: 98° [Hartmann and Gattermann, *Ber.*, **25**, 3531 (1892)]; 101° [Baker and Carruthers, ref. 6]; 103° [Witt, *Ber.*, **21**, 321 (1888)].

(27) Fries, *ibid.*, **54**, 709 (1921).

(28) Fries and Schimmelschmidt, *ibid.*, **58**, 2835 (1925).

(29) Cason and Prout, THIS JOURNAL, **66**, 46 (1944); Cason, *ibid.*, **68**, 2078 (1946); *Chem. Rev.*, **40**, 15 (1947).

3-methoxy-2-acetonaphthone as a pale yellow oil, b. p. 173–174° (8 mm.), which on cooling formed white crystals (lit. b. p. 210–212° (20 mm.)[28]).

This methoxy ketone was demethylated[28] and the crude product crystallized three times from hexane to afford bright yellow crystals of **3-hydroxy-2-acetonaphthone**, m. p. 110.0–111.8°; lit. m. p.'s: 112°,[6,28,30] 121°.[17a]

1-Hydroxy-2-naphthaldehyde was prepared by Rosenmund reduction of 1-acetoxy-2-naphthoyl chloride followed by hydrolysis.[4] The steam distilled product was fractionated to constant m. p. from dry ligroin to yield pale green crystals, m. p. 53.2–54.2° (cor.). Because of its low m. p. (lit. m. p.'s: 59°,[31] 59–60°,[4] 55°[7a]) this compound was analyzed.

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.82; H, 4.89.

A stock sample of **2-hydroxy-1-naphthaldehyde** was thrice recrystallized (charcoal) from ethanol to yield buff colored needles, m. p. 81.7–82.2°; lit. m. p.'s: 81°,[32] 81–82°,[7a] 82°,[31a] 82.2–82.5°.[4]

3-Hydroxy-2-naphthaldehyde was prepared by Rosenmund reduction of 3-acetoxy-2-naphthoyl chloride followed by hydrolysis[4] and thrice recrystallized from aqueous ethanol to produce bright yellow crystals, m. p. 96.3–96.8°; lit. m. p.'s: 97–98°,[4] 98–98.5°,[7a] 99–100°.[33]

Methyl 1-hydroxy-2-naphthoate was prepared by esterifying 1-hydroxy-2-naphthoic acid (Eastman Practical) with methanol and sulfuric acid. The ester was twice recrystallized (charcoal) from ethanol to yield light tan crystals, m. p. 76.5–78° (cor.); lit. m. p.'s: 76–77°,[34] 78°,[35] wet m. p. 76–77.5° (cor.) with some solid remaining up to 95°; depression 0.5°.

Methyl 2-Hydroxy-1-naphthoate.—This compound was prepared by the action of diazomethane on 2-hydroxy-1-naphthoic acid, which was prepared by a modification of Pearl's procedure[36] for oxidizing *p*-hydroxybenzaldehyde to the corresponding acid:

A solution of 34.0 g. (0.200 mole) of silver nitrate in 50 ml. of water was added at 52° to a vigorously stirred solution of 34.4 g. (0.200 mole) of 2-hydroxy-1-naphthaldehyde in 500 ml. of water containing 67.3 g. (1.2 moles) of potassium hydroxide. Hydrogen slowly was evolved, and some heat was generated, for the stirred mixture required four hours to cool to room temperature. After stirring overnight, the mixture was heated to 60°, let to cool to room temperature and stirred for an additional three days. During this time gas evolution slowly continued. The silver was filtered off and the filtrate acidified with sulfur dioxide. In order to avoid the peptization which accompanied filtration and washing, the resulting flocculent suspension was extracted twice with ether and the extract cautiously treated with 10% aqueous sodium bicarbonate solution. The alkaline layer was separated and acidified with hydrochloric acid. The resulting suspension was extracted twice with ether. After washing several times with water, the ether solution was dried over sodium sulfate. Flash distillation of the ether at reduced pressure left pure 2-hydroxy-1-naphthoic acid as a pinkish solid which after vacuum drying over phosphorus pentoxide melted, on quick heating, at 162.5–164° with evolution of carbon dioxide; wt., 17.1 g. (45.5%); lit. m. p.'s: 156–157° on quick heating,[35] 150°,[37] 146°,[38] 157–158°.[34]

From the ether extract left after the above sodium bicarbonate treatment 14.8 g. (43%) of crude, unchanged 2-hydroxy-1-naphthaldehyde was recovered, m. p. 69–81°.

The use of sodium hydroxide instead of potassium hydroxide in this oxidation produced a much lower yield, presumably due to the decreased solubility of both the aldehyde and acid sodium salts. The silver oxide oxidation gave much larger yields than the alkaline oxidation procedure of Kauffmann.[37]

An attempted esterification by pouring a solution of 2-hydroxy-1-naphthoic acid in 100% sulfuric acid into absolute methanol[39] was completely unsuccessful. Esterification by refluxing in methanolic sulfuric acid was impractical due to the ease of decarboxylation of the hydroxyacid. Treatment of the silver salt with methyl iodide produced a crude ester which was purified only through a tedious fractional crystallization. The use of diazomethane proved eminently successful.[40]

An ethereal solution of diazomethane (prepared from 8.2 g. of nitrosomethylurea) was added portionwise to an agitated solution of 8.0 g. (0.043 mole) of 2-hydroxy-1-naphthoic acid in 100 ml. of ether. When addition of a small portion of diazomethane no longer caused immediate and vigorous evolution of nitrogen, a few drops of acetic acid were added to destroy any excess diazomethane. An excess of 10% sodium bicarbonate solution was added and the layers separated. The ethereal layer was washed to neutrality with water and dried over sodium sulfate. Removal of the ether left 7.4 g. (85%) of cream-colored solid, m. p. 73.5–76.5°. Two recrystallizations from aqueous ethanol (charcoal) left 5.1 g. of pure ester, m. p. 78.1–78.9°; lit. m. p.'s: 76°,[35] 77°,[41] 80°.[42]

Acidification of the above bicarbonate extract followed by ether extraction permitted the recovery of 0.9 g. (11%) of unchanged 2-hydroxy-1-naphthoic acid, m. p. 152–156°.

Stock **methyl 3-hydroxy-2-naphthoate** was recrystallized (charcoal) from methanol containing a little water. The pure ester melted at 73–74° (cor.); lit. m. p.'s: 73–74°,[8] 72°[41]; wet m. p. 71–72° (cor.); depression 2°.

α-**Acetonaphthone** was prepared and purified through the picrate.[43] Two distillations produced a pale yellow oil, b. p. 296.5–298°; lit.[43] b. p. 295–297° (745 mm.). Stock β-**acetonaphthone** was twice recrystallized from ethanol, yielding white crystals, m. p. 53.9–54.8° (cor.).

α-**Naphthaldehyde** was prepared by applying the modified Sommelet reaction to α-chloromethylnaphthalene (Eastman Practical, redistilled) according to Badger's directions for α-bromomethylnaphthalene.[44] Purification through the bisulfite adduct followed by two distillations produced a pale yellowish oil, b. p. 148.5° (10 mm.); lit. b. p.'s: 158–159° (14 mm.),[45] 150° (13 mm.),[44] 150–152° (13 mm.).[46] β-**Naphthaldehyde** was prepared by Rosenmund reduction of β-naphthoyl chloride.[47] The distilled aldehyde was recrystallized from aqueous ethanol and then from water to yield white crystals, m. p. 60.4–61.2°; lit. m. p.'s: 59°,[48] 59.5°,[49] 60.5–61°.[50] **Methyl α-naphthoate** was prepared by introducing dry hydrogen chloride into a solution of α-naphthoic acid in dry methanol. The oil obtained on removal of the solvent was taken up in ether. The ethereal solution was washed with water, 10% aqueous sodium bicarbonate solution, and again with water. Evaporation of the dried extract left an oil which refused to solidify on long cooling.[51] Methyl β-naphtho-

---

(30) Wahl, *Compt. rend.*, **206**, 521 (1938).

(31) (a) Bezdzik and Friedlaender, *Monatsh.*, **29**, 375 (1908); (b) Weil and Ostermeier, *Ber.*, **54**, 3217 (1921).

(32) Rousset, *Bull. soc. chim.*, [3] **17**, 300 (1897); Gattermann and Horlacher, *Ber.*, **32**, 284 (1899).

(33) Boehm and Profft, *Arch. Pharm.*, **269**, 25 (1931).

(34) Rodionov, *Bull. acad. sci. U. R. S. S., Classe sci. Chim.*, No. 3, 421–425 (1940); *C. A.*, **35**, 5101 (1941).

(35) Schmitt and Burkard, *Ber.*, **20**, 2699 (1887).

(36) Pearl, *J. Org. Chem.*, **12**, 85 (1947).

(37) Kauffmann, *Ber.*, **15**, 804 (1882).

(38) Kerkhof, *Rec. trav. chim.*, **51**, 755 (1932).

(39) Newman, This Journal, **63**, 2431 (1941).

(40) Procedure suggested by Dr. L. E. Miller.

(41) Meyer, *Monatsh.*, **22**, 777 (1901).

(42) Tijmstra and Eggink, *Ber.*, **39**, 14 (1906).

(43) Lock, *Monatsh.*, **74**, 77 (1943).

(44) Badger, *J. Chem. Soc.*, 535 (1941).

(45) Rupe and Brentano, *Helv. Chim. Acta*, **19**, 581 (1936).

(46) Mayer and Sieglitz, *Ber.*, **55**, 1835 (1922).

(47) Hershberg and Cason, *Org. Syntheses*, **21**, 84 (1941).

(48) Schulze, *Ber.*, **17**, 1527 (1884).

(49) Battershall, *Ann.*, **168**, 114 (1873).

(50) Bamberger and Boekmann, *Ber.*, **20**, 1115 (1887).

(51) Lauer [*ibid.*, **70B**, 1288 (1937)] reported this ester as a solid, m. p. 59.5°, while Koelsch and Hoffman [This Journal, **65**, 989 (1943)] reported a b. p. of 167–169° (20 mm.).

ate was prepared as above and recrystallized from methanol to yield white leafy crystals, m. p. 76.7–78° (cor.); lit. m. p.'s: 77°,[52] 77.8°.[53]

Stock **acetophenone** was twice distilled; b. p. 198–199°. *o*-**Hydroxyacetophenone** (Eastman White Label) was twice distilled; b. p. 109–110° (32 mm.); n^{20}_D 1.5585. A sample of distilled **benzaldehyde**, which had been stored over hydroquinone, was twice redistilled (nitrogen atmosphere); b. p. 71.8–72° (21.5 mm.). Stock **salicylaldehyde** was twice redistilled; b. p. 194°; n^{20}_D 1.5729. **Methyl benzoate** (Eastman White Label) and stock **methyl salicylate** were each redistilled twice; b. p.'s: 193–193.5 and 216–217°, respectively. Phenol (Baker and Adamson Reagent) was distilled twice; b. p. 179–180°. Stock α-**naphthol** was twice recrystallized (charcoal) from aqueous ethanol and then from water (charcoal); m. p. 94.8–95.3° (cor.). Stock β-**naphthol** was thrice recrystallized (charcoal) from water; m. p. 120–121.2°.

Acknowledgments.—The author takes pleasure in thanking the Atomic Energy Commission for the fellowship on which this work was performed. The author is grateful to Dr. C. S. Marvel for valuable advice throughout the course of the work and for providing every possible laboratory facility. Without the aid of Miss Elizabeth Petersen, who determined and helped interpret most of the spectra, and Mrs. Agatha Johnson, who determined some of the spectra, this work would not have been possible. Thanks also are due Dr. E. D. Amstutz for many helpful discussions.

Summary

1. An improved apparatus for the cryoscopic determination of molecular weights in naphthalene solution was used to show that chelated disubstituted naphthalenes exhibit the cryoscopic behavior characteristic of chelated benzene derivatives. This method failed to reveal any differences in the strength of chelation among isomeric 1,2-, 2,1-and 3,2-disubstituted naphthalenes.
2. Infrared spectra were used to show that chelation in 1,2- and 2,1-disubstituted naphthalenes is of about equal strength and considerably greater than in the isomeric 2,3-disubstituted naphthalenes. This result was interpreted as evidence for the proposition that the C_1–C_2 bond of naphthalene has greater than 50% double bond character and that the C_2–C_3 bond has less than 50% double bond character.
3. Infrared spectra were used to show that chelation in a given *o*-disubstituted benzene has a strength intermediate between that of the analogous 1,2- (or 2,1-) and 2,3-disubstituted naphthalenes. This result was explained as a consequence of the relative degrees of bond fixation in the parent hydrocarbons.
4. The acid dissociation constants of salicylaldehyde and the three *o*-hydroxynaphthaldehydes were correlated with the degree of conjugation between substituents.
5. The utility of a knowledge of bond fixation in correlating the infrared spectra of certain compounds was demonstrated.

URBANA, ILLINOIS RECEIVED AUGUST 11, 1949

---

(52) Vieth, *Ann.*, **180**, 305 (1876); Stohmann, Kleber and Langbein, *J. prakt. Chem.*, [N. F.] **40**, 341 (1889).

(53) Lauer, ref. 51.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity.[1] III. Aminolysis of Esters with Primary Amines[2]

BY EDWARD MCC. ARNETT[3], JOHN G. MILLER AND ALLAN R. DAY

The first investigations in this series[4] dealt with the ammonolysis of esters. In these studies the influence of alkyl and aryl groups present in the esters and the catalytic effects of various solvent media were measured. While detailed investigation of the ammonolysis reaction is being continued, it has been advantageous to extend the scope of these studies by taking up the aminolysis of esters, a reaction whose kinetics have been studied previously by only a few workers.[5]

This investigation has profited from the studies of ammonolysis. Thus, for example, from the earlier work in this series it was possible to predict a suitable standard medium and a single ester for comparison of the reactivities of the series of primary amines studied.

The results show clearly the effect of both the basicity of the amines and their bulks and shapes, as well as the catalytic activity of hydroxylated compounds.

Experimental

The experimental procedure was essentially that used in the earlier investigations.[4] The unreacted amine in any reaction system was determined by titration with half-normal hydrochloric acid, back-titration being carried out with half-normal sodium hydroxide with methyl red as indicator. Addition of ethylene glycol or dioxane to the extent of 50% of the volume of the sample titrated, or addition of sodium chloride to a concentration of 2 molar did not affect the end-point. Hydrolysis of the esters or amides during the titration was considered negligible because no change in the end-point color was observed when several of the systems were allowed to stand for long periods after titration and were later heated to boiling.

---

(1) From a thesis submitted in April, 1949, by E. McC. Arnett in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented at the Philadelphia Meeting of the Division of Organic Chemistry, American Chemical Society, April, 1950.

(3) du Pont Fellow, 1948–1949.

(4) (a) Gordon, Miller and Day, THIS JOURNAL, **70**, 1946 (1948); (b) Gordon, Miller and Day, *ibid.*, **71**, 1245 (1949); (c) Gordon, Dissertation, University of Pennsylvania, 1948.

(5) Glascoe, Kleinberg and Audrieth, *ibid.*, **61**, 2387 (1939); *ibid.*, **63**, 2965 (1941); Grunfeld, *Compt. rend.*, **194**, 893 (1932); Vavon and Bourgeois, *ibid.*, **202**, 1446, 1593 (1936).