[CONTRIBUTION FROM THE U. S. BUREAU OF MINES, CENTRAL EXPERIMENT STATION]

Steric Hindrance and Short Wave Length Bands in the Ultraviolet Spectra of Some Naphthalene and Diphenyl Derivatives[1]

BY R. A. FRIEDEL,[2] MILTON ORCHIN[3] AND LESLIE REGGEL[3]

Introduction

The aromatic cyclodehydrogenation studies being conducted in this Laboratory have provided a series of compounds that exhibit interesting relationships between ultraviolet absorption spectra and steric hindrance. Most of the work on the correlation of steric hindrance with ultraviolet spectra has been done on diphenyls,[4,5,6] but Jones[7,8,9] has studied more complex aromatic systems. He observed, for example, that in 9-phenylanthracene and 9,10-diphenylanthracene, the phenyl groups cannot be coplanar with the anthracene nucleus because of hindrance between neighboring hydrogen atoms. The resultant lack of coplanarity is manifested by the similarity of the spectra to that of anthracene. Jones[8] has noted the general effects of steric hindrance on the spectra of conjugated ring systems, such as increased fine structure, hypsochromic band shifts, and decreased intensity. The present paper discusses these effects as observed for several naphthalene and diphenyl derivatives, which were investigated down to 206 mμ.

Discussion and Results

Dinaphthyls.—The spectra of the three dinaphthyls[10] are shown in Fig. 1. 1,1′-Dinaphthyl (I) shows the greatest effect of steric hindrance as its spectrum is closest to that of naphthalene (Fig. 3); however, some resonance structures involving coplanarity probably exist, since fine structure is diminished. 2,2′-Dinaphthyl (II) should be free of steric hindrance; its spectrum shows a type of structure radically different from that of naphthalene with a very strong band at 254, a weaker broad band at 305, and a short wave length band at 212 mμ. 1,2′-Dinaphthyl (III) is, as expected, intermediate between the other two. Its spectrum is more similar to that of 1,1′-dinaphthyl (I); however, intensities are greater, fine structure is diminished, and bands are considerably broader than in (I).

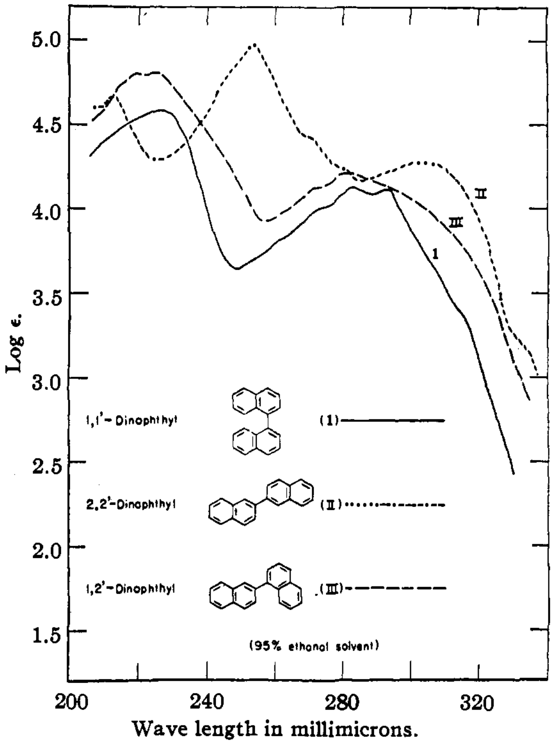

Fig. 1.

The spectrum of a dinaphthyl derivative,[11] 2,2′7,7′-tetramethyl-1,1′-dinaphthyl (IV) (Fig. 2), indicates very strong steric hindrance. Fine structure is developed, including the appearance of the typical naphthalene band at 319 mμ, and intensities are approximately double those of naphthalene. Also shown is the spectrum of a hydrogenated derivative, 3,4,3′,4′-tetrahydro-1,1′-dinaphthyl (V). Coplanarity is probably lacking in this compound also since the spectrum is very similar to that of 1,2-dihydronaphthalene.

Phenylnaphthalenes.—The spectra[12] of naphthalene (VI), 1-phenylnaphthalene (VII), and 2-phenylnaphthalene (VIII) are shown in Fig. 3. The 1-phenylnaphthalene (VII) spectrum resembles that of naphthalene, indicating strong steric hindrance; however, bathochromic shifts and greatly decreased fine structure indicate appreciable contribution from coplanar resonance

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[4] O'Shaughnessy and Rodebush, THIS JOURNAL, 62, 2906 (1940).

[5] Pickett, Walter and France, *ibid.*, 58, 2296 (1936).

[6] Pestemer and Mayer-Pitsch, *Monatsh.*, 70, 104 (1937).

[7] R. N. Jones, THIS JOURNAL, 63, 313, 1658 (1941).

[8] R. N. Jones, *ibid.*, 67, 2127 (1945).

[9] R. N. Jones, *Chem. Rev.*, 32, 1 (1943).

[10] Adams and Kirkpatrick, THIS JOURNAL, 60, 2180 (1938), determined the spectra of 1,1′- and 2,2′-dinaphthyl to 230 mμ. They found a band at 297 in 2,2′- which we do not find. Their low wave length band for 1,1′- is at 238, whereas ours lies at 226.

[11] Jones, THIS JOURNAL, 67, 2127 (1945), determined the spectrum of 2,2′-diamino-1,1′-dinaphthyl.

[12] Jacobs, Craig and Lavin, *J. Biol. Chem.*, 141, 51 (1941), determined the spectra of 1- and 2-phenylnaphthalene down to 235 mμ.

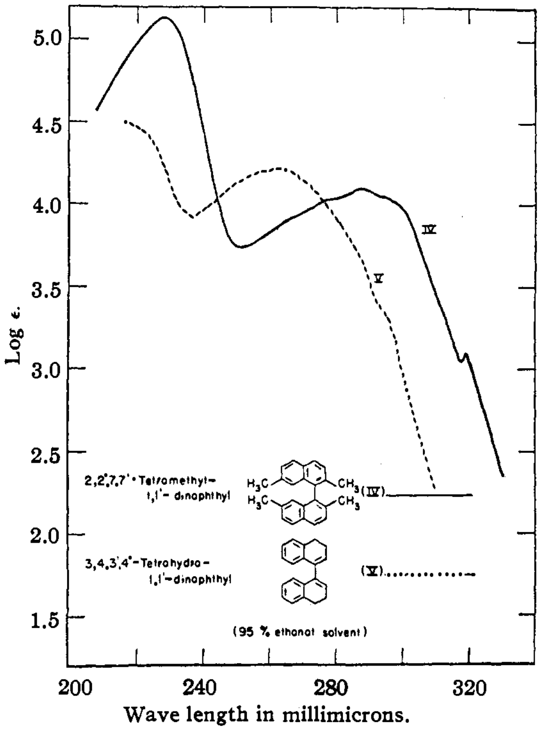

Fig. 2.

structures. The aromatic rings of 2-phenylnaphthalene (VIII), on the other hand, can assume a coplanar structure; accordingly the spectrum of this compound is quite different from that of naphthalene. The same bands observed by Jacobs, *et al.*, for (VIII) are found at 250 and 285; in addition a short wave length band appears at 212 mμ. Thus the general form of the spectrum of (VIII) is the same as that of unhindered 2,2'-dinaphthyl (II) (Fig. 1).

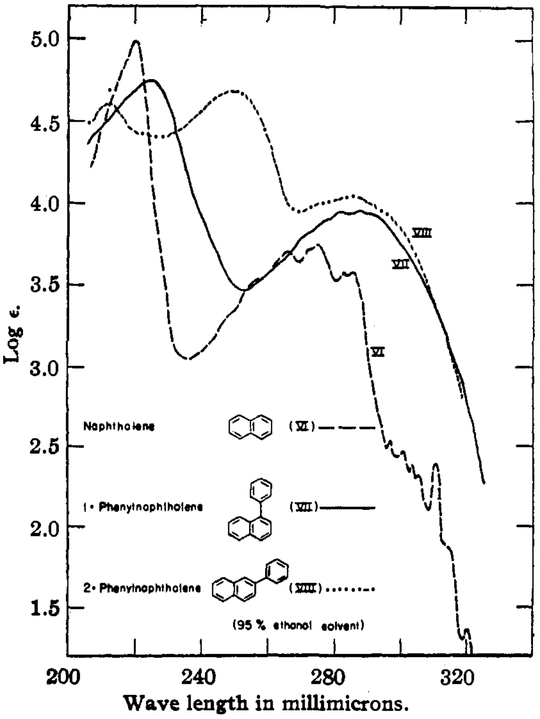

Fig. 3.

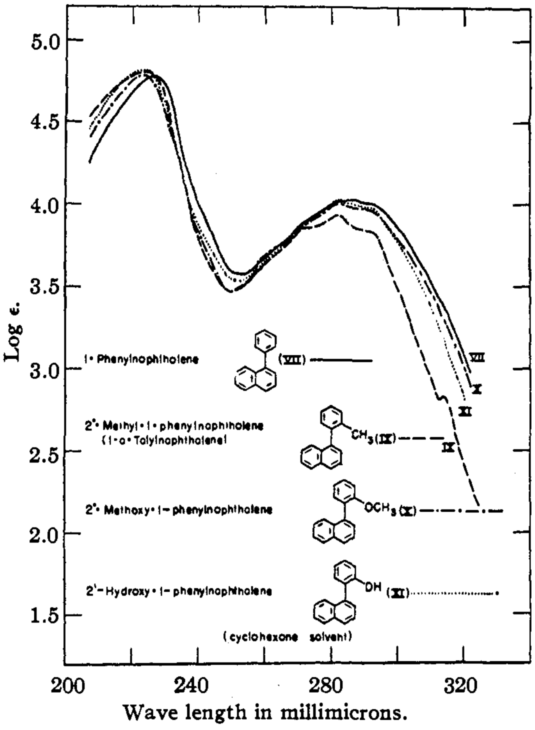

Fig. 4.

The spectra in Fig. 4 of 1-phenylnaphthalene (VII) and three of its derivatives, 2'-methyl-1-phenylnaphthalene (1-*o*-tolylnaphthalene) (IX), 2'-methoxy-1-phenylnaphthalene (X) and 2'-hydroxy-1-phenylnaphthalene (XI), show the effects of substituting the groups —CH_3, —OCH_3 and —OH, respectively, in the ortho position of the phenyl group of 1-phenylnaphthalene (VII). The methyl group in 1-*o*-tolylnaphthalene (IX) appreciably increases steric hindrance since its presence produces in the 280 mμ region a weaker, narrower band with typical naphthalene fine structure, including the band at 314 mμ. The methoxyl (X) and hydroxyl (XI) groups apparently cause only slight additional hindrance over that already present in 1-phenylnaphthalene (VII); the bands as a whole are somewhat narrower and definite peaks are produced at 282 and 283, respectively, giving band structures similar to that of the strongly hindered methyl derivative (IX). All of these spectra were determined in both 95% alcohol and cyclohexane. Differences are very slight if any, but the spectra shown were obtained in cyclohexane in order to remove any effect of a polar solvent.

The spectra of 2-phenylnaphthalene (VIII) and two of its derivatives, 2'-methyl-2-phenylnaptha-

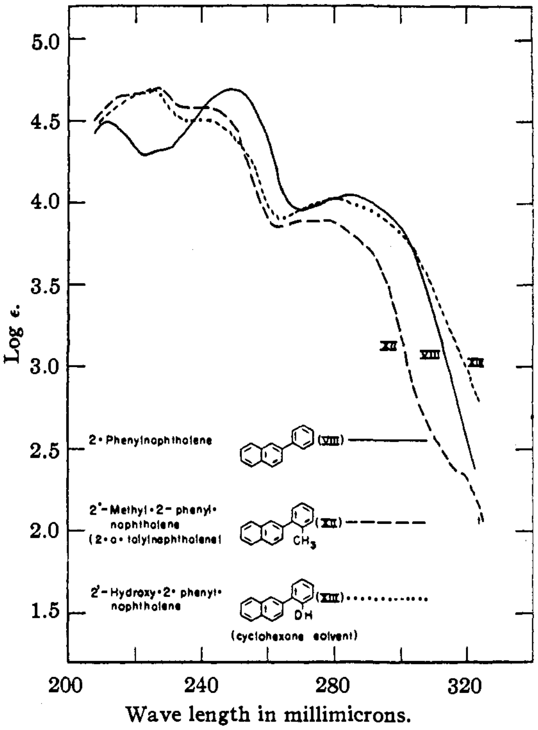

Fig. 5.

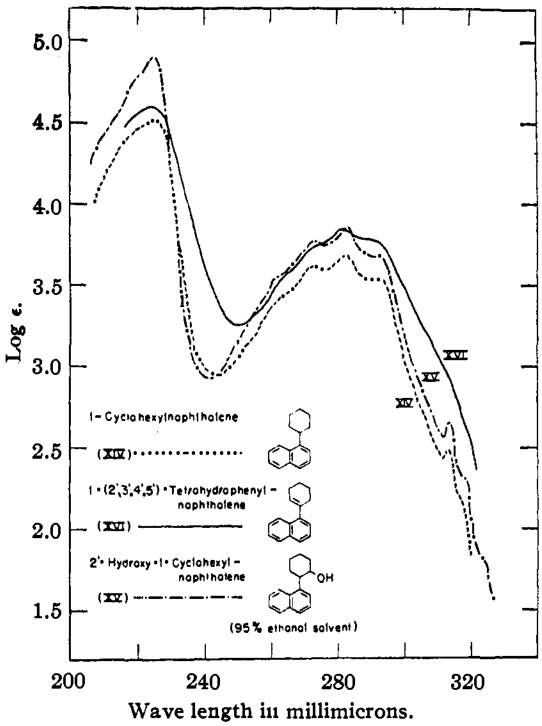

Fig. 6.

lene (2-*o*-tolylnaphthalene) (XII) and 2′-hydroxy-2-phenylnaphthalene (XIII) are given in Fig. 5 to permit comparison of the relative degrees of steric hindrance produced by the groups $-CH_3$ and $-OH$, in the ortho position of the phenyl group of unhindered 2-phenylnaphthalene. The methyl group, in 2-*o*-tolylnaphthalene (XII), again causes the greater steric hindrance; instead of the two 2-phenylnaphthalene bands at 250 and 212, one wide band with a doublet splitting occurs around 230 mμ. Further, the long wave length band undergoes a hypsochromic shift from 286 to 274 mμ. The spectrum of the hydroxyl derivative (XIII) exhibits the same spectral structure as (XII) indicating a surprising amount of hindrance due to the hydroxyl group. The wide long wave length band at 280 does not shift with respect to the same band in 2-phenylnaphthalene, probably because of a phenoxy contribution; in a polar solvent, 95% ethanol, this band is shifted 10 mμ to longer wave lengths and is considerably broader.

Other Naphthalene Derivatives.—The spectra of 1-cyclohexylnaphthalene (XIV), 2′-hydroxy-1-cyclohexylnaphthalene (XV) and 1-(2′,3′,4′,5′-tetrahydrophenyl)-naphthalene (XVI) are shown in Fig. 6. The first two compounds produce spectra typical of naphthalene derivatives with one saturated substituent; their spectra are almost identical with that of strongly hindered 1-*o*-tolylnaphthalene (IX). The spectrum of the tetrahydro compound (XVI), in which the naphthalene nucleus is conjugated with one double bond, shows the usual band widening, decreased fine structure, and increased intensity which accompany conjugation.

Diphenyls.—The spectra of diphenyl (XVII) and three of its derivatives, 2-methyldiphenyl (XVIII), 2-methoxydiphenyl (XIX) and 2-hydroxydiphenyl (*o*-phenylphenol) (XX) (Fig. 7) exhibit the effect of $-CH_3$, $-OCH_3$ and $-OH$, in an ortho position of diphenyl. The methyl group in (XVIII) has the greatest effect with the 248 diphenyl band shifting to 235 mμ and the intensity decreasing appreciably. The same band in the spectrum of the methoxy derivative (XIX) shifts only 2 mμ to 246, which indicates very slight hindrance; but the decrease in intensity is significant. The hydroxyl group in *o*-phenylphenol (XX) appears to have an even greater effect; in cyclohexane solvent the 248 band shifts 3 mμ to 245 and the decrease in intensity is quite large. For (XIX) and (XX) in 95% ethanol, however, intensities of the band coincide and band positions are reversed; 2-methoxydiphenyl (XIX) is not affected by the polarity of the solvent, but for *o*-phenylphenol (XX) the band shifts from 245 to 246.5. The bands at 284 in the spectra of both oxygenated compounds are phenoxy bands.

Comparison of Diphenyls and Naphthalenes.—Diphenyl and its derivatives were investigated principally because of the similarity in the 250 mμ region between diphenyl (XVII) and the related unhindered naphthalenes, 2-phenylnaphthalene (VIII) and 2,2′-dinaphthyl (II). Since these compounds also produce bands at 212 mμ, diphenyl was investigated in the same region;

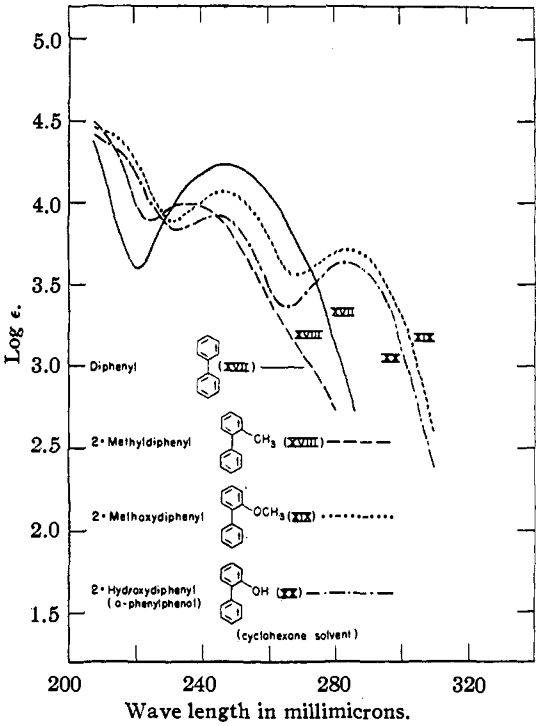

Fig. 7.

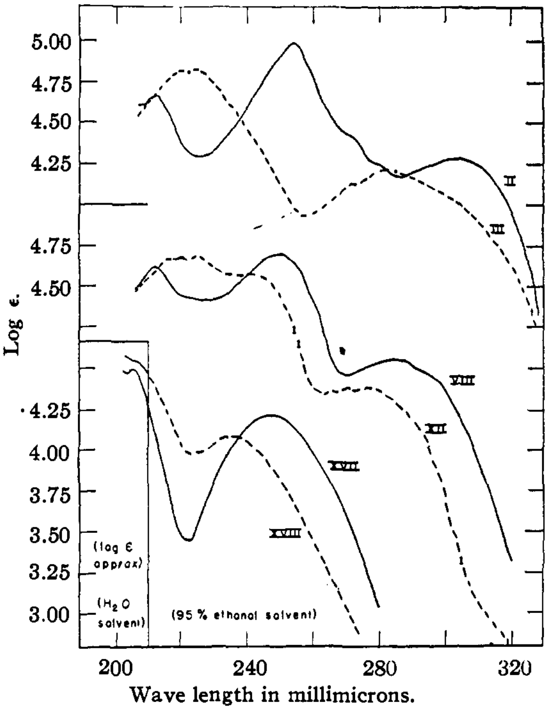

Fig. 8.—Comparison of diphenyls and naphthalenes. Convergence of bands with steric hindrance. Curves: (II) 2,2′-dinaphthyl, (III) 1,2′-dinaphthyl, (VIII) 2-phenylnaphthalene, (XII) 2-*o*-tolylnaphthalene, (XVII) diphenyl and (XVIII) 2-methyldiphenyl.

using water as a solvent at short wave lengths a new small band is found at 205 mμ.[13] The spectrum is given in Fig. 8 together with the spectra of (II) and (VIII).

Similarities in steric hindrance effects for the three compounds, (II), (VIII) and (XVII), are shown by plotting with each of them the spectra of the related sterically hindered derivatives, 2-methyldiphenyl (XVIII), 2-*o*-tolylnaphthalene (XII) and 1,2′-dinaphthyl[14] (III) (Fig. 8). In all three cases the 250 mμ bands of the respective parent compounds undergo hypsochromic shifts and decreased intensities with introduction of hindrance. On the other hand, the short wave length bands in the 210 mμ region appear to sustain bathochromic shifts and thus to converge toward the shifted 250 mμ bands. The effect is greater for the hindered naphthalene derivatives.

Spectrophotometry

The customary limit of the Beckman spectrophotometer used, with good absolute ethanol, is around 220 mμ. As is well known, this solvent always contains troublesome traces of benzene which are difficult to remove. Purification is simplified and the limit of the instrument reduced to 216 mμ by merely using 95% ethanol; this solvent has already come into general use. The limit is further reduced to 206 mμ by substituting for the original 2,000 megohm grid resistor in the phototube amplifier a 20,000 megohm, essentially noise-free, resistor.[15] A 10,000 megohm resistance results in a limit of 208 mμ. Increased resolution also results from these substitutions as seen in the spectra of naphthalene in Fig. 9; the decreased band widths made possible by such resistors are compared at one wave length. It is apparent from these curves, especially in the 305 mμ region that the 20,000 megohm resistor has effected some increased resolution over that obtained with 10,000 megohms. The former resistor was used throughout this investigation but because of the sluggishness of the galvanometer the latter is preferable for general use.

The lowest wave length attained for solutions is 202 mμ. with water as solvent. Water was resorted to in the short wave length measurements of diphenyl and methyldiphenyl since no bands are found down to 206 mμ, the limit of the instrument with 95% ethanol as solvent. Although the solubility of these compounds in water is very slight, it is found to be more than enough to make measurements in this region of intense absorption. For gases the lowest wave length attainable is slightly below 200 mμ, the end of the wave length scale.

In these regions of the spectrum scattered energy is a large percentage of the small total energy transmitted by the glass envelopes on hydrogen

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[13] Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936), reported a small band for diphenyl vapor in the vacuum ultraviolet at 203 mμ.

[14] 1,2′-Dinaphthyl was used to show this steric effect in lieu of a hindered methyl derivative of 2,2′-dinaphthyl.

[15] Made by Victoreen Instrument Company, Cleveland, Ohio.

tube and phototube. Appropriate corrections for this scattered energy were applied to all spectra. Reliability of the low wave length bands reported is substantiated by the detection of the 207 and 203.5 mμ fine structure bands for benzene solution,[15a] found by Henri.[16] These bands were also observed on a borrowed Beckman which was modified for checking purposes by inserting a 20,000 megohm resistor in the amplifier.

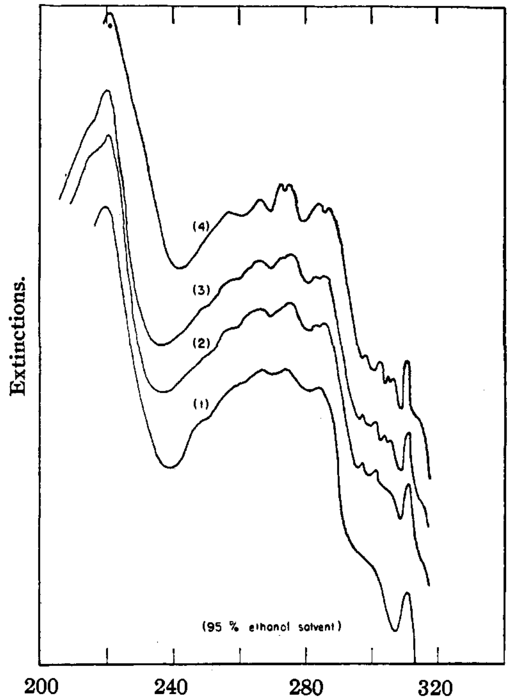
Preparation of Compounds[17]

The preparation of 1,2′-dinaphthyl, 2,2′-dinaphthyl, 1-(2′,3′,4′,5′-tetrahydrophenyl)-naphthalene, 1-cyclohexylnaphthalene, 1-phenylnaphthalene,[18] 1,1′-dinaphthyl,[19] and 2-methyldiphenyl[20] have been described previously. The 2,2′,7,7′-tetramethyl-1,1′-dinaphthyl and 3,3′,4,4′-tetrahydro-1,1′-dinaphthyl were gifts of Professor M. S. Newman. *o*-Phenylphenol was a gift of the Dow Chemical Company and was purified by recrystallization, melting point 56.6–57.8°. The diphenyl was an Eastman Kodak Co. product which was chromatographed to remove fluorescent impurities and then recrystallized, melting point 68.5–69.4°. 2-Methoxydiphenyl[21] was prepared by Mr. E. O. Woolfolk by the methylation of *o*-phenylphenol with diazomethane. It was purified by chromatography, followed by recrystallization from petroleum ether and had melting point 28.8–29.4°. Semimicro methoxyl determination (E. O. W.) gave 16.6% methoxyl (calcd. 16.9). The preparation of 2′-hydroxy- and 2′-methoxy-1-phenylnaphthalene and 2′-hydroxy-2-phenylnaphthalene will be described in a future publication.

2-Phenylnaphthalene.[22]—1-Phenylnaphthalene (5.06 g.) was passed over silica gel at 405–460° during twenty minutes in the apparatus previously described.[23] The product (4.57 g.) was twice crystallized from alcohol and gave 1.0 g. of 2-phenylnaphthalene as colorless crystals, m. p. 102.4–103.8°. The sample used for ultraviolet absorption spectrum measurements was carefully purified by chromatographic adsorption on alumina.

The complex with *s*-trinitrobenzene was obtained from ethanol as yellow plates, m. p. 113.5–115.2° with sintering at 111°. *Anal.*[24] Calcd. for $C_{22}H_{15}N_3O_6$: N, 10.07; for $C_{28}H_{18}N_6O_{12}$: N, 13.33. Found: N, 12.8, 12.7. The analysis indicates that the complex of *s*-trinitrobenzene with 2-phenylnaphthalene is formed in the ratio of 2 moles of the nitro compound to one of the hydrocarbon. The complex is readily dissociated and difficult to purify. 2-Phenylnaphthalene did not form a complex with picric acid when solutions of both components were mixed in the usual fashion.

1-*o*-Tolylnaphthalene.—To the Grignard reagent from 1.1 mole of *o*-bromotoluene and 1.21 moles of magnesium in 725 cc. of ether, there was added 1.0 mole of 1-tetralone[25] in 150 cc. of ether. The mixture was stirred and refluxed for sixteen hours, then decomposed with ammonium chloride solution. The ether layer was separated and dried. Evaporation of the ether left a mixture of crystals and oil which was filtered. The crystalline material was washed with cold petroleum ether and was obtained as colorless needles (34 g.). This material was investigated separately, and the results will be reported later. The filtrate containing the oil and petroleum ether was fractionally distilled. There was collected 64.12 g., b. p. 90–115° (1 mm.), of a first fraction which was nearly all recovered tetralone; 41.97 g., b. p. 115–142° (0.7 mm.); and a third fraction, b. p. 130–230° (0.3 mm.) which was a gum. The second fraction was redistilled from sodium and gave as a main fraction, 31.99 g., b. p. 130–138° (1 mm.). *Anal.*[26] Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 91.2; H, 7.5. This crude 1-(*o*-tolyl)-3,4-dihydronaphthalene (29.25 g.) was heated with 1.5 g. of 30% palladium-on-charcoal catalyst.[27] There was evolved 2720 cc. (N. T. P.) of hydrogen (91.3%). The product was distilled and 28.25 g. of material which solidified on cooling was collected. One crystallization from methanol gave 22.73 g. of colorless needles, m. p. 68.8–70.8°. The sample for ultraviolet absorption spectrum measurements was carefully purified by chromatographic adsorption on alumina.



Wave length in millimicrons.

Fig. 9.—Spectra of naphthalene under varying resolving power. Amplifier grid resistance, R, and the usable band widths (B. W.) at 285 mμ are: (1), R = 2000 MΩ, B. W. = 13.6 Å.; (2), R = 10,000 MΩ, B. W. = 6.8 Å.; (3), R = 20,000 MΩ, B. W. = 5.1 Å.; (4), comparison curve from Mayneord and Roe, *J. Chem. Soc.*, 929 (1934).

2-*o*-Tolylnaphthalene.—To the lithium compound from 20.0 g. of 2-bromonaphthalene, 1.47 g. of lithium wire, 95 cc. of ether and 25 cc. of benzene there was added 11.9 g. of *o*-methylcyclohexanone in 45 cc. of ether. After four and one-half hours of refluxing with stirring the green mixture was decomposed with ice water. The organic layer was separated, dried and the solvents evaporated. The residual oil was heated at 160–170° for half an hour with 14 g. of potassium bisulfate. The

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(15a) NOTE ADDED IN PROOF: Detection of these benzene bands in water solution was reported by Doub and Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

(16) Henri, "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 359.

(17) All melting points corrected.

(18) Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947).

(19) Orchin and Friedel, *ibid.*, **68**, 573 (1946).

(20) Orchin, *ibid.*, **67**, 499 (1945).

(21) Hönigschmidt, *Monatsh.*, **22**, 570 (1901).

(22) Mayer and Schiffner, *Ber.*, **67B**, 67 (1934).

(23) Orchin, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 673 (1945).

(24) Microanalysis by Dr. T. S. Ma, University of Chicago, Chicago, Illinois.

(25) We wish to thank Dr. Gilbert Thiessen and the Koppers Co. for a generous sample of 1-tetralone.

(26) Macroanalysis by Coal Analysis Section, U. S. Bureau of Mines.

(27) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

product was taken up in benzene, and the benzene evaporated. Distillation of the residue gave a first fraction which was discarded and a second fraction, b. p. 132–150° (0.4 mm.) weighing 11.13 g. This oil was heated with 1.00 g. of palladium-on-charcoal catalyst[27] at 320–360° for two hours during which time 1513 cc. (N. T. P.) of hydrogen (67.5%) was evolved. The material was distilled, and the distillate dissolved in petroleum ether and chromatographed on alumina. The least strongly adsorbed material was discarded (small amount of naphthalene), and the balance of the product with the exception of some very strongly absorbed material recovered. Crystallization from methanol gave 2.80 g. of colorless crystals, m. p. 44.7–46.6°. The pure sample used for ultraviolet absorption spectrum measurements had m. p. 45.7–48.0°.

Anal.[28] Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.5; H, 6.6.

2-*o*-Tolylnaphthalene did not form complexes with picric acid or 2,4,7-trinitrofluorenone[29] when solutions of the two components were mixed in the usual manner. A concentrated solution of the hydrocarbon and *s*-trinitrobenzene in alcohol gave a first crop of *s*-trinitrobenzene. The mother liquor precipitated bright yellow crystals, m. p. 101.2–102.5°, which were shown by analysis to contain one mole of the hydrocarbon to two moles of the nitro compound.

Anal.[29] Calcd. for $C_{29}H_{20}N_6O_{12}$: N, 13.04. Found: N, 13.1.

Acknowledgments.—The authors wish to acknowledge the helpful suggestions of Drs. J. J. McGovern and E. Solomon and the loan of the former's instrument for checking purposes. Thanks are due Lois Pierce and Ruth Borgman, who determined the spectra.

Summary

Steric hindrance effects are discussed in connection with the spectra of 1,1′-, 1,2′- and 2,2′-dinaphthyl, 1- and 2-phenylnaphthalene, diphenyl and various derivatives of some of these compounds. Short wave length peaks are detected in the region 205 to 212 mμ for compounds containing two aromatic ring systems conjugated without steric hindrance. These bands and the longer wave length bands appear to converge toward each other when the coplanarity of the systems is hindered by introduction of interfering groups.

All spectra were determined to 206 mμ on a Beckman spectrophotometer; two spectra were measured to 202 mμ. The simple methods for attaining this limit, as well as increased resolution, are described.

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(28) Microanalysis by Arlington Laboratories, Fairfax, Virginia.

(29) Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Kinetics of Neutralization of Nitroethane with Ammonia and Methylamines

BY RALPH G. PEARSON

The rates of neutralization of the simple nitroparaffins with hydroxyl ion and other charged bases have been measured by several investigators.[1] The reaction is a slow process conveniently

$$R_1R_2CHNO_2 + B^- \longrightarrow R_1R_2CNO_2^- + BH \quad (1)$$

measured at 0° in water solution. This paper reports the rates of neutralization of nitroethane with ammonia, methyl-, dimethyl- and trimethylamine in aqueous solution at 0 and 5.2°. The reactions were followed by the change in conductance as the ions were formed

$$CH_3CH_2NO_2 + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3CHNO_2^- + BH^+ \quad (2)$$

where B stands for the neutral base and BH^+ for the conjugate acid.

The work was undertaken both to obtain fundamental data on the kinetics of ionization of neutral molecules in a solvent of high dielectric constant and to see how the rates for the various amines correlate with their base strengths. The increased basicity of methylamine and dimethylamine compared with ammonia and the sharp decrease in base strength for trimethylamine have been the subject of several papers.[2]

Experimental

Preparation of Materials.—Commerical Solvents nitroethane was dried with magnesium sulfate, refluxed with urea, dried with phosphorus pentoxide and fractionated through a 10-plate column. Small middle portions boiling within a 0.1° range were taken for use. The organic amines were obtained from Eastman Kodak Co. white label hydrochlorides or amines converted to hydrochlorides. The salts were recrystallized from water and the amines freed by adding measured amounts of sodium hydroxide and distilling in all glass carbon dioxide-free apparatus into conductivity water. For methylamine and dimethylamine, one-third of the amount of sodium hydroxide needed was added and the distillate discarded, another one-third of sodium hydroxide was added and the distillate collected. For trimethylamine the distillate from the first one-third equivalent of sodium hydroxide was collected. Ammonia was obtained by distilling C. P. ammonia into conductivity water. Solutions were made up 0.05 to 0.10 molar as determined by titration and stored in a carbon dioxide-free apparatus connected to a buret. Solutions of nitroethane were made up by direct weighing, adding conductivity water and storing in a cold room until used.

Apparatus.—Conductances were measured with a modified Jones–Josephs bridge[3] using an oscilloscope for a null point indicator. This combination of direct reading

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(1) (a) Pedersen, *Kgl. Danske Videnskab. Selskab., Math-fys. Medd.,* **12**, No. 1 (1932); (b) Junell, Dissertation, Upsala, 1935; (c) Maron and La Mer, THIS JOURNAL, **60**, 2588 (1938).

(2) (a) Wynne-Jones and Everett, *Proc. Roy. Soc.* (*London*), **A177**, 499 (1941); (b) Brown, THIS JOURNAL, **67**, 374, 378 (1945).

(3) Dike, *Rev. Sci. Inst.*, **2**, 379 (1931).