hours. In some runs, following the method of Martin,[6] the addition of toluene and acetic acid gave excellent results.

3-Phenyl-5-alkylsalicylic Acids.—The method described by Vorozhtsov and Troshchenko[7] for the carboxylation of *o*-phenylphenol was used for the introduction of carbon dioxide into *p*-alkyl-*o*-phenylphenols. The preparation of a typical 3-phenyl-5-alkylsalicylic acid is described.

An intimate mixture of 14 g. of *p*-propyl-*o*-phenylphenol and 95 g. of finely powdered anhydrous potassium carbonate was introduced into a steel tube of 180 ml. capacity and 18 g. of dry-ice was added. The tube was heated at 110° for one hour and the temperature was raised 10° per hour until 200° was reached. After one hour the temperature was raised to 225° and maintained for fourteen hours. The tube was cooled and the contents were poured into a beaker. Two hundred ml. of water was added and the mixture was acidified with concentrated hydrochloric acid. The oil which first formed solidified to a gummy solid. The precipitate was filtered and recrystallized once from acetic acid and water. The yield was 8.29 g. or 49% of theoretical, melting 127–136°. On further purification the product melted 137–143.5°.

3-Phenyl-5-ethylsalicylic acid was prepared similarly in excellent yield. However, by the same general method only a very low yield of 3-phenyl-5-*n*-hexylsalicylic acid was obtained. This low yield may be due to the high molecular weight and corresponding insolubility of the potassium salt of *p*-hexyl-*o*-phenylphenol or, as Harris and Christiansen[3] suggest, to the diminution of the acidic character of the phenol as the alkyl group increases in size.

The 3-phenyl-5-alkylsalicylic acids prepared were practically insoluble in water but were quite soluble in alcohol, benzene, ether, and glacial acetic acid. All dissolved in dilute alkali.

Acetyl - 3 - phenyl - 5 - alkylsalicylic Acids.—3-Phenyl-5-ethylsalicylic acid and 3-phenyl-5-*n*-propylsalicylic acids were acetylated with acetyl chloride and acetic acid. The excess acetyl chloride and most of the acetic acid were removed by evaporation below 75°, finally in partial vacuum. For purification, the acetyl derivatives were dissolved in absolute alcohol and precipitated by the addition of ice and ice water. This procedure would not remove unacetylated 3-phenyl-5-alkylsalicylic acid or this product formed on hydrolysis of the acetylated derivative, so the melting points reported likely are slightly in error. The above acetyl-3-phenyl-5-alkylsalicylic acids are insoluble in water. They dissolve readily in ether, alcohol, benzene, and dilute alkali.

Summary

3-Phenyl-5-ethylsalicylic acid, 3-phenyl-5-*n*-propylsalicylic acid, and 3-phenyl-5-*n*-hexylsalicylic acid were made by the carboxylation of *p*-ethyl-, *p*-*n*-propyl-, and *p*-*n*-hexyl-*o*-phenylphenol, respectively.

RICHMOND, VA. RECEIVED JUNE 17, 1940

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[6] Elmore L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[7] Vorozhtsov and Troshchenko, *C. A.*, **32**, 7907 (1938); *J. Gen. Chem.* (U. S. S. R.), **8**, 424–429 (in English, 430) (1938).

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

Infrared Absorption Studies of Some Hydrocarbons

BY F. T. WALL AND G. W. MCMILLAN

Spectroscopic studies of various hydrocarbons have shown that the valence vibrations associated with C–H bonds have absorption wave lengths in the neighborhood of 3.3 μ. Considerable variation in the wave lengths is observed, however, although one important general effect was noticed by Bonino.[1a] He pointed out that the wave lengths for aromatic C–H bonds were usually lower than those for the aliphatic type. The same effect was observed by Buswell, Rodebush and Roy.[1b] This experimental generalization suggests that one could use absorption frequencies as a spectroscopic criterion for aromatic character.

For example, infrared absorption studies of the phenylmethanes demonstrated clearly the presence or absence of aliphatic and aromatic hydrogens. It was found[2] that molecules such as benzene and tetraphenylmethane, which have only aromatic hydrogens, showed absorption peaks in the neighborhood of 3.25 μ which could be attributed to aromatic carbon–hydrogen bond vibrations. It also was found that toluene, di- and triphenylmethanes[2,3] likewise showed absorption in the 3.25 μ region which could be assigned to their aromatic hydrogens. In addition, however, the latter molecules showed absorption in the neighborhood of 3.45 μ which was absent in the case of benzene and tetraphenylmethane. Accordingly the peaks in the 3.45 μ region were attributed to modes of vibration involving for the most part aliphatic carbon–hydrogen bonds.

The phenylmethane series provided a relatively

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[1] (a) G. B. Bonino, *Trans. Faraday Soc.*, General Discussion, 879 (1929); (b) Buswell, Rodebush and Roy, THIS JOURNAL, **60**, 2444 (1938).

[2] F. T. Wall and G. W. McMillan, *ibid.*, **61**, 1053 (1939).

[3] J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A167**, 257 (1938).

simple set of molecules to interpret because their structural formulas enable one to classify the hydrogens without ambiguity. However, certain more complex molecules including those with condensed ring systems are known to be chemically less aromatic than benzene even though they possess no portion that could be called aliphatic with certainty. It was accordingly felt desirable to study such compounds by spectroscopic means, the results to be interpreted by using the phenyl methanes as standards of comparison.

Substances Used.—The molecules here considered are biphenyl, naphthalene, anthracene, phenanthrene, indene, hydrindene, tetralin, *cis-unsym*-octahydrophenanthrene and 9,10-dihydrophenanthrene. Considerable care was taken to obtain pure materials. Synthetic naphthalene and anthracene and technical biphenyl were subjected to sublimation and crystallization procedures for their purification. Commercial phenanthrene was purified by the method of Durland and Adkins[4] and technical grade tetralin was fractionated in a six-foot (1.8-m.) column to constant boiling point and constant index of refraction. Indene and hydrindene were likewise subjected to fractionation until a constant boiling point and constant refractive index were obtained.

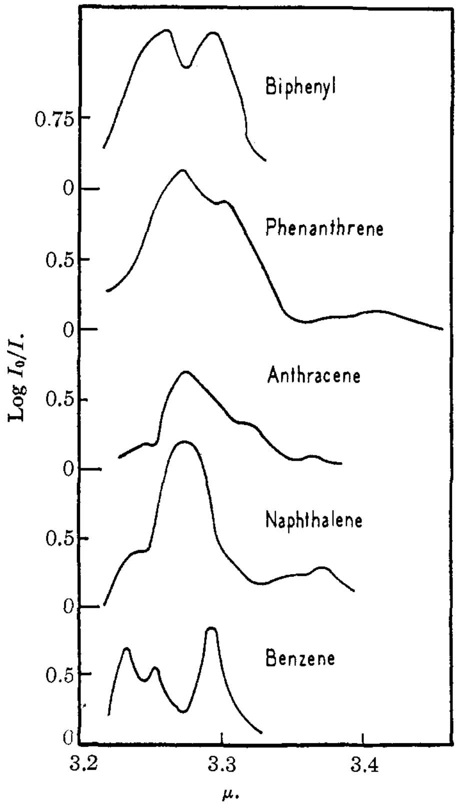

Fig. 1.—Log I_0/I for solutions of benzene, naphthalene, anthracene, phenanthrene and biphenyl.

Experimental Results

The technique employed has been described previously.[1,5] Carbon tetrachloride solutions of the materials were used and the absorption measured by means of a grating spectroscope. The molar absorption coefficients were then computed by means of the equation

$$K = \frac{1}{cd} \log \frac{I_0}{I}$$

where c is the concentration, d the length of the absorption cell and I_0/I the ratio of galvanometer deflections for the light beam passing through pure solvent and through a similar cell containing the solution.

The results of the absorption studies are shown in Figs. 1 and 2. In Fig. 1 are the absorptions of benzene, napthalene, anthracene, phenanthrene and biphenyl, none of which possess any purely aliphatic parts. Except for anthracene the solutions studied were 0.1 M in cells 0.325 cm. long, whereas the anthracene solution used was 0.05 M, the cell length being 0.647 cm. Of these molecules benzene[6] and naphthalene[7] have been investigated previously but they are included here

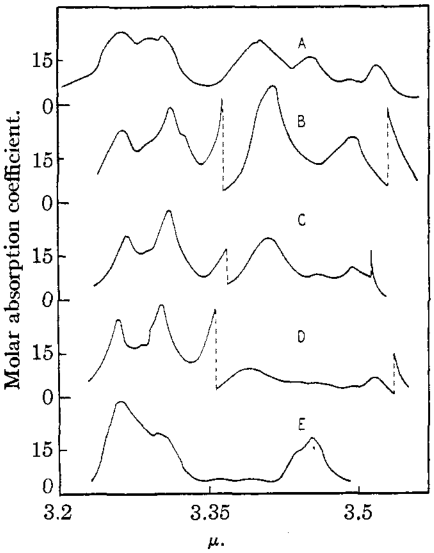

Fig. 2.—Molar absorption coefficients for A, 9,10-dihydrophenanthrene; B, *cis-unsym*-octahydrophenanthrene; C, tetralin; D, hydrindene; E, indene.

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[4] Durland and Adkins, This Journal, **59**, 135 (1937).

[5] Buswell, Dietz and Rodebush, *J. Chem. Phys.*, **5**, 501 (1937).

[6] Leberknight, *Phys. Rev.*, **43**, 967 (1933).

[7] Fox and Martin, *J. Chem. Soc.*, 318 (1939).

for the sake of comparison. In Fig. 2 are plotted molar absorption coefficients for indene, hydrindene, tetralin, *cis-unsym*-octahydrophenanthrene and 9,10-dihydrophenanthrene, all of which have at least one aromatic ring in the molecule. Since the absorptions in the region 3.4 μ were so great for hydrindene, tetralin and *cis-unsym*-octahydrophenanthrene, a change of scale was introduced in the plots as indicated by the dotted lines. The positions of the maxima for both sets of molecules are shown in Tables I and II.

TABLE I

Molecule	Wave Lengths of Absorption Peaks, μ			
Benzene	3.232	3.253	3.291	
Naphthalene		3.243	3.275	3.370
Anthracene	3.247	3.275	3.315	3.363
Phenanthrene		3.271	3.303	3.406
Biphenyl		3.260	3.292	

TABLE II

Molecule	Wave Lengths of Absorption Peaks, μ					
Indene	3.259		3.299		3.454	
Hydrindene	3.259		3.303	3.390		3.518
Tetralin	3.267		3.311	3.410	3.494	
cis-unsym-Octahydrophenanthrene	3.263		3.311	3.414	3.494	
9,10-Dihydrophenanthrene	3.263	3.291	3.303	3.402	3.454	3.518

Discussion of Results

It will be observed that biphenyl like benzene shows absorption only in the 3.25 μ region, which fact is to be correlated with its 100% aromatic nature. Naphthalene, anthracene and phenanthrene all show some absorption on the long wave length side which can be related empirically to their diminished aromatic character as observed in their chemical properties.

The absorption maxima in Fig. 2 easily can be divided into two groups, those in the neighborhood of 3.25 μ and those in the 3.45 μ region. This is similar to what was observed for the phenylmethanes.[2,3] The shorter wave length peaks can be attributed to the aromatic parts of the molecules and the other peaks for the most part to the aliphatic hydrogens. In view of the results for naphthalene, anthracene and phenanthrene, however, one cannot be certain about the assignment of the 3.45 μ peaks for the second group of molecules.

An approximate idea as to the values of the Hooke's law force constants for the different kinds of C–H bonds can be obtained by a simple calculation. For an average value,[2] take

$$k = 4\pi^2 m\overline{\nu^2} \qquad (1)$$

where m is the mass of a hydrogen atom and $\overline{\nu^2}$ is the average square of the various carbon–hydrogen absorption frequencies. In Table III are listed values of k calculated by means of equation (1). For benzene, naphthalene, anthracene, phenanthrene and biphenyl all of the maxima were used for calculating $\overline{\nu^2}$. For the other molecules the maxima were divided into two groups and two constants, aliphatic and aromatic, were calculated.

TABLE III

Molecule	Hooke's law force constant × 10^{-5}, dynes/cm. Aromatic	Aliphatic
Benzene	5.55	
Biphenyl	5.50	
Naphthalene	5.44	
Anthracene	5.41	
Phenanthrene	5.34	
Indene	5.50	4.95
Hydrindene	5.47	4.94
Tetralin	5.46	4.95
9,10-Dihydrophenanthrene	5.46	4.94
cis-unsym-Octahydrophenanthrene	5.45	4.93

It is clear from the values of k that the hydrogens are on the average less tightly bound in naphthalene, anthracene and phenanthrene than they are in benzene. Indene has an aromatic k value practically as large as that for benzene, although hydrindene and tetralin have lower values. This might be expected in view of the Mills-Nixon effect[8] which would tend to render the benzene ring more aliphatic in nature.

Summary

The infrared absorption spectra of a number of hydrocarbons in carbon tetrachloride solution were studied in the 3.35 μ region. The positions of the absorption maxima were correlated with the aromatic and aliphatic properties of the molecules.

URBANA, ILLINOIS RECEIVED MAY 31, 1940

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[8] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).