

the relative importance of two contributing states for molecules other than the hydrogen halides and for states other than ionic and covalent. Where the potential energy curves cross, however, complications are introduced by reason of resonance splitting at such crossing points due to perturbations.

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Summary

Assuming the wave function of a molecule to be given by $\psi = \psi_c + a\psi_i$ where ψ_c and ψ_i are covalent and ionic functions, respectively, the constant a is shown to be determined by

$$a^2 = (W_c - W)/(W_i - W)$$

Values for a^2 are determined empirically and correlated with ionic character and dipole moment values.

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Infrared Absorption of the Phenylmethanes

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Studies of the infrared absorption spectra of various organic molecules have shown that the molecules possess vibrational frequencies more or less characteristic of the bonds that occur in the molecule. Thus, two different molecules with a common group usually will give spectra each possessing bands representative of the group which is present in both molecules. This constancy of frequencies has proved highly useful in interpreting infrared absorption measurements, particularly where structural changes take place. This is possible because frequency shifts can be used as an indication of such changes.

With a view toward distinguishing spectroscopically between aliphatic and aromatic hydrogens, investigations were carried out for a number of hydrocarbons. In this paper there will be reported the results of studies on the phenylmethanes, which are the simplest molecules possessing both aromatic and aliphatic parts. In a subsequent paper, the results for a number of larger aromatic hydrocarbons will be given and the results correlated with the degree of aromatic character.

Substances Used.—The molecules here considered are benzene, toluene, diphenylmethane, triphenylmethane and tetraphenylmethane. Of these molecules, benzene¹ and toluene^{1,2} have been carefully studied previously, but under conditions different from those present in the investigation here reported.

The benzene was Merck reagent benzene, thio-

phene free. A toluene sample was prepared by purifying technical toluene by the method of Schwalbe,³ which removed thiophene and its homologs. The sample subsequently was fractionated and all but a limited portion discarded. The diphenylmethane and triphenylmethane were synthetic products prepared in the organic chemistry laboratories of the University of Illinois. The first three compounds were fractionated to constant boiling point and constant refractive index. For a sample of tetraphenylmethane we are indebted to Professor C. S. Schoepfle of the University of Michigan to whom we express our thanks. It was prepared from triphenylchloromethane and diphenylmagnesium and treated with concentrated sulfuric acid to remove traces of triphenylmethyl peroxide. It was then crystallized from benzene to give a product of high purity.

The absorption was studied for solutions of the substances in carbon tetrachloride by means of a technique previously described.⁴ Except for tetraphenylmethane, the concentrations were kept constant at 0.1 molar and the cell length at 0.325 cm. A saturated solution of tetraphenylmethane was used in a 2-cm. cell. The instrument was a grating spectroscope of high resolution, the grating being of the echelette type with 3600 lines to an inch. A Nernst glower was used as a source of radiation. The absorption curves were investigated in the range 3.2 to 3.6 μ , which covers the region in which carbon-hydrogen vibrations are

(3) C. Schwalbe, *Ber.*, **38**, 2208 (1905).

(4) Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 501 (1937); Borst, Buswell and Rodebush, *ibid.*, **6**, 61 (1938).

(1) R. B. Barnes, *Phys. Rev.*, **36**, 296 (1930).

(2) C. E. Leberknight, *ibid.*, **43**, 967 (1933).

found to occur. The results show that the presence or absence of aliphatic hydrogens can be determined by studies of this type and thus provide a basis for using infrared absorption methods for investigating aromatic character.

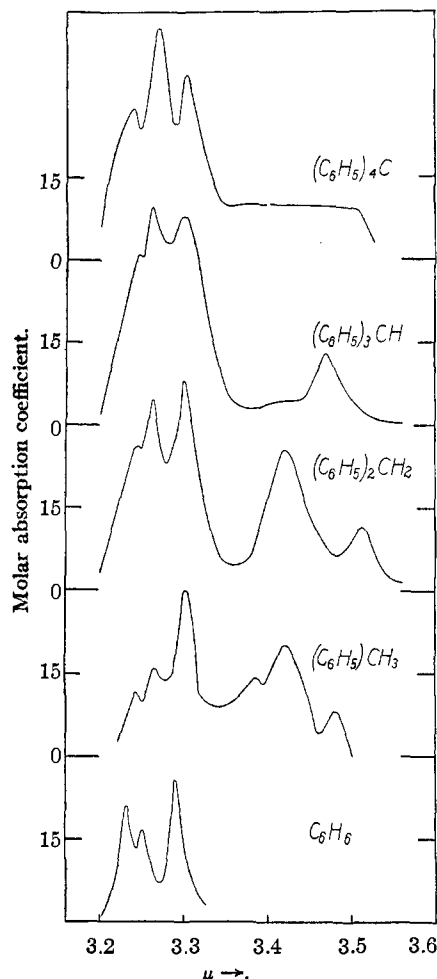


Fig. 1.—Infrared absorption curves for phenylmethanes and benzene in carbon tetrachloride solution.

Discussion of Results.—In Fig. 1 are plotted the absorption curves for the various substances as a function of wave length. For each of the substances except tetraphenylmethane, the ordinates represent molar extinction coefficients defined as

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

where I_0/I is the ratio of intensities of light transmitted by pure solvent and the same length of solution. c is the concentration of the solution in moles per liter and d is the length of the cell in centimeters. For tetraphenylmethane the ordi-

nate scale was adjusted to make the heights of its maxima conform to the general trend.

It will be observed that the absorption peaks can be naturally divided into two groups of wave lengths greater and less than about 3.35μ . Only those molecules with aliphatic hydrogens have absorption peaks in the neighborhood of 3.45μ . It is, therefore, reasonable to suppose that those absorption peaks are due to modes of vibration involving, for the most part, aliphatic carbon-hydrogen bonds. Since all of the molecules have aromatic parts (benzene and tetraphenylmethane being *completely* aromatic) it is natural to assign the absorption peaks in the neighborhood of 3.25μ to aromatic carbon-hydrogen vibrations. The wave lengths corresponding to the maxima are given in Table I. The probable error for the wave lengths is $\pm 0.002 \mu$.

Substance	λ aliphatic μ			λ aromatic μ		
Benzene				3.232	3.253	3.291
Toluene	3.386	3.422	3.482	3.243	3.267	3.303
Diphenylmethane		3.422	3.514	3.247	3.263	3.299
Triphenylmethane			3.470	3.247	3.263	3.299
Tetraphenylmethane				3.240	3.271	3.303

The wave lengths for benzene and toluene absorption maxima are in good agreement with those found by Barnes¹ and Leberknight.² This is true even though those investigators studied the absorption of the pure liquids whereas the results reported here are for solutions in carbon tetrachloride. Slight frequency shifts are to be expected due to the change in medium.

It is interesting to note that the number of aliphatic absorption maxima for the different molecules is equal to the number of aliphatic hydrogens in the molecule. This is readily accounted for by a qualitative vibrational analysis. The aliphatic vibration for $(C_6H_5)_3CH$ is the aliphatic carbon-hydrogen valence vibration with a mode symmetrical with respect to the pseudo three-fold axis of the molecule. It is to be compared with the carbon-hydrogen frequency of chloroform. The aliphatic vibrations for $(C_6H_5)_2CH_2$ are of opposite symmetry characteristics with respect to the plane half way between the hydrogens and passing through the central carbon atom. Both vibrations involve motion in the plane containing the hydrogens and the central carbon atom.

The case of toluene is particularly interesting. If the molecule had a true three-fold symmetry axis such as is present in the methyl halides, it

would possess only two distinct aliphatic carbon-hydrogen frequencies of which one would be doubly degenerate. Owing, however, to the fact that the phenyl group is neither a point particle nor linear, the molecule does not possess a three-fold axis and the frequency which would be degenerate is split into two frequencies. Peaks corresponding to those frequencies occur at 3.386μ and 3.422μ and are broadened due to internal rotation of the two groups. The 3.482μ band is due to a vibration symmetrical with respect to the pseudo three-fold axis.

The aromatic absorption peaks are not as readily assigned. Benzene should have only one infrared active carbon-hydrogen frequency, so the presence of three peaks calls for some explanation. It is quite possible that a splitting takes place because of accidental degeneracy with high states of other frequencies or combinations of other frequencies.

The phenylmethanes, possessing less symmetry than benzene, could easily have three active aromatic carbon-hydrogen frequencies. It is to be noticed that the phenylmethanes all give similar aromatic absorption except for a progressive shift in relative heights of the peaks as the number of phenyl groups is increased.

Although exact vibrational analyses of benzene⁵ have been made, the same for the phenylmethanes is out of the question because of their greater size and lesser symmetry. However, it is reasonable to suppose that for the so-called aliphatic vibrations, bonds other than the aliphatic carbon-hydrogen bonds are not appreciably involved in the motion. A similar statement can be made for the aromatic carbon-hydrogen frequencies. This notion is supported by calculations in connection with some simpler molecules.⁶ In view of that assumption, it is possible to write

$$k = \frac{4\pi^2 m}{n} \sum_{i=1}^n \nu_i^2$$

where k is the Hooke's law force constant for one

(5) E. B. Wilson, *Phys. Rev.*, **45**, 706 (1934); R. C. Lord and D. H. Andrews, *J. Phys. Chem.*, **41**, 149 (1937).

(6) F. T. Wall, *THIS JOURNAL*, **60**, 71 (1938).

type of carbon-hydrogen bond, m the mass of the hydrogen atom, n the number of frequencies in the class under consideration (aliphatic or aromatic) and $\sum_{i=1}^n \nu_i^2$ the sum of the squares of those frequencies. This equation is justified in the light of the assumption made because the diagonal terms of the secular equation are of the form $4\pi^2 \nu^2 - \frac{k}{\mu}$ where μ is a reduced mass (here taken to be the mass of the hydrogen atom). The calculated Hooke's law force constants for the molecules here considered are given in Table II.

TABLE II

Molecules	Hooke's law constant, $\times 10^{-5}$ dynes/cm.	
	Aromatic	Aliphatic
Benzene	5.55	
Toluene	5.50	5.00
Diphenylmethane	5.50	4.89
Triphenylmethane	5.50	4.89
Tetraphenylmethane	5.50	

Although the absolute values of the constants in Table II are not very significant owing to the approximations made, the relative values are of more importance. It is clear that hydrogens are more tightly bound to aromatic carbons than they are to aliphatic carbons. It is not to be inferred from this that aromatic hydrogens should be less reactive than aliphatic hydrogens since many other factors enter in which influence reactivity. It is also to be noticed that the aromatic hydrogens in the phenylmethanes all have the same force constant, but with a value slightly less than for benzene.

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Summary

The infrared absorption spectra of the phenylmethanes and benzene have been investigated in the range 3.2 – 3.6μ . The results are correlated with the structures of the molecules and force constants are calculated for the different carbon-hydrogen bonds.

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