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Molecular Distortion and Electronic Spectrum of Aromatic Compounds. I. Chlorinated Derivatives of Alkylbenzenes[1]

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The absorption electronic spectrum of pentachlorobenzene (I), perchlorobenzene (II), 2,3,4,5,6-pentachlorotoluene (III), 2,3,4,5,6-pentachloro-1-chloromethylbenzene (IV), 2,3,4,5,6-pentachloro-1-dichloromethylbenzene (V), 2,3,4,5-tetrachloro-1-trichloromethylbenzene (VI), 2,3,5,6-tetrachloro-1-trichloromethylbenzene (VII), perchlorotoluene (VIII), perchloroethylbenzene (IX), 1,4-bistrichloromethylbenzene (X), 2,5-dichloro-1,4-bistrichloromethylbenzene (XI), perchloro-*p*-xylene (XII) and pentamethyltrichloromethylbenzene (XIII) from 200 mμ to the visible region, are reported and discussed. Those compounds having trichloromethyl groups flanked by two *ortho* chlorine atoms show abnormal spectra, consisting chiefly in great bathochromic shifts of some of their bands from their "expected" places, which is accounted for in terms of molecular distortion.

Introduction

Most of the steric effects on electronic spectrum in organic chemistry are caused by steric inhibition of resonance which determines hypsochromic displacements of the bands assigned to the affected chromophoric system. In the study of the highly chlorinated alkylbenzenes here reported important bathochromic shifts due to steric causes were found.

Results and Discussion

In Table I data concerning the electronic absorption spectra of some polychlorinated alkylbenzenes from 200 mμ to the visible region, are given.

TABLE I

Name	λmax, mμ	ε × 10^{-3}
Pentachlorobenzene (I)	298	0.39
	289	0.37
	219	21.5
Perchlorobenzene (II)	298	0.23
	291	0.25
	232	19.0
	222	26.0
2,3,4,5,6-Pentachlorotoluene (III)	293	0.17
	286	0.21
	219	20.5
2,3,4,5,6-Pentachloro-1-chloromethylbenzene (IV)	306	0.64
	295	0.58
	225	29.3
2,3,4,5,6-Pentachloro-1-dichloromethylbenzene (V)	308	1.12
	297	0.94
	225	33.5
2,3,4,5-Tetrachloro-1-trichloromethylbenzene (VI)	302	0.84
	292	0.80
	221	34.0
2,3,5,6-Tetrachloro-1-trichloromethylbenzene (VII)	316	2.1
	221	30.0
Perchlorotoluene (VIII)	319	1.42
	223	35.0
Perchloroethylbenzene (IX)	319	2.05
	224	41.0
1,4-Bistrichloromethylbenzene (X)	283	0.96
	275	1.00
	237	16.0
	211	6.5
2,5-Dichloro-1,4-bistrichloromethylbenzene (XI)	302	1.95
	294	2.00
	242	11.0
	219	31.0
Perchloro-*p*-xylene (XII)	365	3.00
	280	6.6
	236	25.5
	219	27.0
Pentamethyltrichloromethylbenzene (XIII)	303	1.40
	250	7.4
	218	31.0

Smith and Turton have reported the ultraviolet absorption spectra of some polychlorinated aromatic derivatives.[2] However, some of their data have been found to be erroneous. At least in the case of perchloro-*p*-xylene the error is presumably a misprint.[3]

The ultraviolet spectra here reported are divided in "normal" and "abnormal." Common features of these two classes are: A low absorption band, with a value for the maximum extinction of 0.2–3.0 × 10^3, and a complex, high absorption band at shorter wave lengths with its highest maximum at 220–240 mμ, with an extinction of 15–40 × 10^3. These bands are going to be called the "secondary" and the "principal" bands, respectively.[4]

The "normal" spectra (substances I, II, III, IV, V, VI, VII, X and XI) have the essential features found in other benzene derivatives (Fig. 1, V, VI). The secondary and the principal bands are obviously the so-called B and E bands, respectively, of benzene and its derivatives. As expected, due to the high ring substitution, in the present cases the secondary band is greatly displaced bathochromically. Its usually rich fine structure is here limited to two peaks separated 7–11 mμ from each other. The principal band is also shifted by substitution, and in most of the cases looks unsymmetrical because of the presence of a shoulder on the side of longer wave lengths. This shoulder is usually located at 235–250 mμ. In some cases, as in the *p*-bistrichloromethylbenzenes, there is no shoulder but a new maximum in its place (see Fig. 2, XI). This new band is going to be called the "first principal" band.[4]

On the other side, 2,3,5,6-tetrachloro-1-trichloromethylbenzene (VII), perchlorotoluene (VIII), perchloroethylbenzene (IX) and perchloro-*p*-xylene (XII) show "abnormal" spectra (Fig. 1, VIII; Fig. 2, XII). The secondary band is deprived of its fine structure and its maximum is located at an abnormally high wave length. Perchloro-*p*-xylene (XII) is the most remarkable example (it is yellow because its secondary band, λ 365 mμ, steps into the visible region). Although the second principal band of these compounds remains in the neighborhood of 220–230 mμ, the first principal band—as a shoul-

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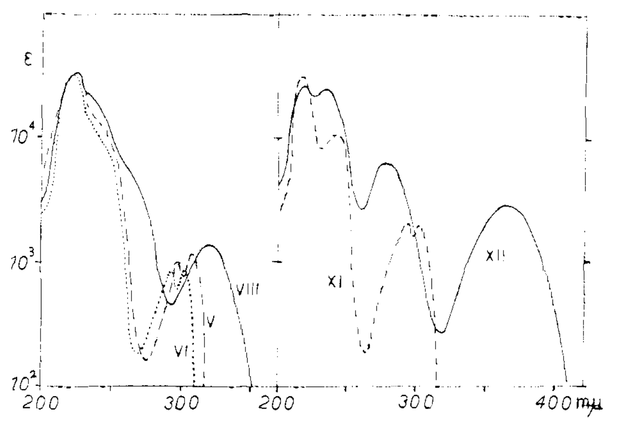
[1] This work has been sponsored by the Air Research and Development Command, United States Air Force, under the contract AF 61(052)-141.

[2] F. Smith and L. M. Turton, *J. Chem. Soc.*, 1350 (1955).

[3] M. Ballester, C. Molinet and J. Castañer, THIS JOURNAL, preceding paper.

[4] L. Doub and J. M. Vanderbelt, *ibid.*, **69**, 2714 (1947).



Wave length, mμ.

Fig. 1. Fig. 2.

der or as a maximum—is also greatly shifted toward longer wave lengths. In VIII and IX it is a shoulder at around 265 and 255 mμ, respectively. In XII it is a maximum at 280 mμ.

Introduction of a chlorine atom in a benzene ring usually displaces the secondary band bathochromically by a few (less than 10) mμ, the shift being less the greater the number of resident chlorine atoms.[5] The same seems to occur with the introduction of chlorine atoms in the methyl group of toluene.[6] However, replacement of the last hydrogen atom in VI and V to give VIII causes shifts of 22 and 17 mμ, respectively (see Fig. 1). The effect of the replacement by chlorine of the last two hydrogen atoms of XI to give XII is most dramatic. The total shift is then 67 mμ, *i.e.*, an average of 33.5 mμ per chlorine atom (see Fig. 2).

The "abnormal" compounds have at least a trichloromethyl group flanked by two *ortho* chlorine atoms. A substance having such a structure is provided with a large steric strain caused by the strong interactions between the two *ortho* chlorine atoms and those of the trichloromethyl group, and consequently its molecule is distorted. Evidence for this has been advanced.[3]

Distortion raises the energy of both ground and excited states of the molecule. However, due to the greater anti-bonding character of the excited states their energies are less affected by distortion. Consequently, it can be expected that the ultraviolet spectra would show their bands shifted bathochromically with respect to the normal, unstrained compounds of comparable structure and degree of substitution. Owing to the high number of nodal planes of the B_{2u} state it can be presumed that the secondary band which is associated to the forbidden $A_{1g} \rightarrow B_{2u}$ electronic transition would be much affected. In fact, in the abnormal compounds it is shifted from 20 to 60 mμ from what can be called its expected place. These shifts represent energies from 5.5 to 15 kcal./mole. As far as the "first principal" band is concerned, in perchloro-*p*-xylene (XII), for example, it is displaced bathochromically about 30 mμ, *i.e.*, 12.5 kcal./mole.

In a 2,6-dichloro-1-dichloromethylbenzene as well as in a 2-chloro-1-trichloromethylbenzene the dichloro- or the trichloromethyl groups in spite of their bulkiness are arranged so as to give a low-distortion molecule.[3]

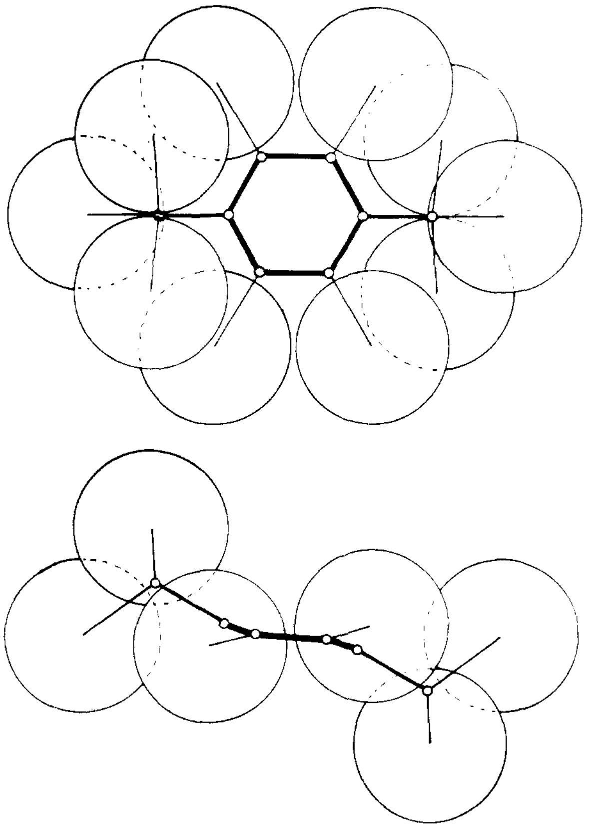


Fig. 3.

The most energetically favorable arrangement for the trichloromethyl group in a 2,6-dichloro-1-trichloromethylbenzene appears to be the one in which two α-chlorine atoms lie on one side and the third one the other side of the mean plane of the benzene ring.[3] In Fig. 3 the top and the side view of the distorted molecule of perchloro-*p*-xylene are shown. With such an arrangement very little interaction takes place between the *ortho* chlorine atoms and that third α-chlorine atom. It is reasonable that this position of minimum interaction will be occupied by the trichloromethyl group of perchloroethylbenzene (IX). Consequently, in spite of the pentachloroethyl group being much bigger than the trichloromethyl group, this compound should not be substantially more strained than VIII. Accordingly, the secondary band of both perchloroaralkanes is located about in the same place.

Brown and co-workers[7] have calculated the strain of the ground state of the homomorphs[8] of 2,6-dichloro-1-trichloromethylbenzene. Their value, 24 kcal./mole, represents therefore an upper limit for the bathochromic shifts of a 2,6-dichloro-1-trichloromethylbenzene due to steric strain, which is consistent with the data here reported.

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[5] H. Conrad-Billroth, *Z. physik. Chem.*, **B19**, 76 (1932).

[6] W. F. Hammer and F. A. Matsen, THIS JOURNAL, **70**, 2482 (1948).

[7] H. C. Brown, D. Gintis and L. Domash, *ibid.*, **78**, 5387 (1956).

[8] Homomorphs of a compound are obtained by replacement of substituents by others of similar sizes,[7] *i.e.*, methyl groups for chlorine atoms.

Cram and co-workers[9] have studied the ultraviolet absorption spectra of the paracyclophanes and closely related compounds. Some of them must be greatly distorted and show great bathochromic shifts of the B-band. In these cases, the benzene ring must adopt a "boat-like" conformation.

Ingraham concluded that the shift of the secondary band of the strained paracyclophanes are mostly due to 2pσ interaction between rings.[10] His conclusion was based much on the appearance of a first principal band which is also found in the strained derivatives here studied, where no such interaction can take place.

In view of the results here reported one is inclined to consider that the great shifts found also in the cyclophanes are mostly due to benzene ring warping.

Pentamethyltrichloromethylbenzene (XIII), a homomorph of VIII, has been recently reported.[11] Its ultra-violet absorption spectrum (see Table I) is "abnormal." There is no fine structure of the secondary band, and it is located about 20 mμ away from its "expected" place.[12]

According to Platt[14] it is possible to assign to each benzene substituent a vector called spectroscopic moment, from which the maximum extinction may be calculated. This calculation fails, however, with most of the highly substituted benzene derivatives here studied. However, some interesting sequences that can be drawn from it agree with the data: examples: 1, I < III < IV < V < VIII < XII; 2, VI < VIII < VII; 3, VI < XI; 4, X < XI < XII.

Experimental

An Uvispek Hilger Spectrophotometer was used. Benzene-free cyclohexane was the solvent. All the substances but pentamethyltrichloromethylbenzene were obtained in this Laboratory and were purified by recrystallization from the suitable solvents until they melted sharply, and dried under high vacuum. The 2,3,4,5,6-pentachloro-1-chloromethylbenzene and 2,3,4,5,6-pentachloro-1-dichloromethylbenzene, which usually contaminate each other, were purified by chromatography on alumina grade A.

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[9] D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6132 (1954).

[10] L. L. Ingraham, *J. Chem. Phys.*, **18**, 988 (1950); M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 498–501.

[11] R. J. Rolih, unpublished preparation; see H. Hart and R. W. Fish, THIS JOURNAL, **80**, 5894 (1958).

[12] Due to the smaller substituent effect of the methyl group in polymethylbenzenes the secondary band is found at shorter wave lengths. Examples: Pentamethylbenzene,[13] 269, 275, 279 mμ, *vs.* pentachlorobenzene, 289, 299 mμ. Hexamethylbenzene,[13] 270, 279 mμ, *vs.* hexachlorobenzene, 291, 298 mμ.

[13] H. Conrad-Billroth, *Z. physik. Chem.*, **B29**, 170 (1935).

[14] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Intermediates and Transition States in Reactions of Allylic and Homoallylic Systems. I. Free Energy Relationships in the Reactions of α-Aryl-γ-methylallyl and α-Methyl-γ-arylallyl *p*-Nitrobenzoates

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p-Nitrobenzoate esters of α-aryl-γ-methylallyl and α-methyl-γ-arylallyl alcohols have been solvolyzed in aqueous dioxane solutions of varying composition. All of the esters investigated solvolyzed by uncatalyzed first-order processes involving alkyl–oxygen fission. In the case of the α-aryl esters, solvolysis (k_S) was accompanied by a concurrent, intramolecular, first-order rearrangement (k_R) to the allylic isomer. In 70 volume per cent. aqueous dioxane the rates of these competing reactions were nearly equal. The total rate of reaction ($k_S + k_R$) of each of the α-aryl isomers was found to be *ca.* 325 greater than the solvolysis rate of the corresponding γ-aryl ester. Substitution of a *p*-methyl substituent into the phenyl ring of the solvolyzing esters furnished a rate enhancement of *ca.* 10.0 in the case of each of the measured rate constants (k_S, k_R) of the α-phenyl ester and *ca.* 8.4 for the solvolysis of the allylic γ-phenyl ester. The reactions of the four esters under investigation showed relatively large solvent sensitivities, a change in solvent from 70 to 60 volume per cent. aqueous dioxane enhancing the reaction rates by factors of *ca.* 3.2 ($m \simeq 0.7$) for the rearrangement processes, k_R, and of *ca.* 4.0–5.0 ($m \simeq 0.85$–1.0) for the hydrolysis reactions. The kinetic results permit a calculation of the ground state free energy differences between pairs of allylic isomers. The γ-aryl esters (which contain a styrene-type chromophore) are found to be 3.2 ± 0.1 kcal./mole more stable than the isomeric α-aryl esters. The greatly enhanced rates of reaction of the α-aryl isomers over their isomers are due chiefly to this difference in ground state energies.

Introduction

In recent years a number of investigations of solvolysis reactions of isomeric allylic halides and esters have uncovered some interesting facets of carbonium ion behavior. A paper by Young, Winstein and Goering[1] reported that the first-order acetolysis of α,α-dimethylallyl chloride is accompanied by an essentially intramolecular rearrangement to the isomeric γ,γ-dimethylallyl chloride. These authors preferred to interpret their results in terms of a common ion-pair intermediate produced from either isomeric chloride and capable of giving rise either to covalent chlorides by internal return or to solvolysis product. de la Mare and Vernon[2] have also investi-

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[1] W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951).

[2] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 2504 (1954).