Tetrahedron, 1964. Vol. 20, pp. 2217 to 2227. Pergamon Press Ltd. Printed in Northern Ireland

THE ULTRAVIOLET SPECTRUM OF ALKYL BENZENES

EVIDENCE FOR CARBON-HYDROGEN AND CARBON-CARBON BOND HYPERCONJUGATION (BAKER-NATHAN EFFECTS)*

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(*Received* 23 *January* 1964; *in revised form* 25 *March* 1964)

Abstract—By means of the theory of the migration moment of the substituents the absorption of the secondary band ($^1A_{1g} \rightarrow {}^1B_{2u}$ transition) of sixty-seven alkyl benzenes has been studied. The hyperconjugation effects of the carbon-hydrogen and carbon-carbon bonds as well as those of the vibrational and static symmetry perturbations of the benzene nucleus are evaluated.

INTRODUCTION

THE delocalization of σ bonds of alkyl substituents was suggested by Baker and Nathan in 1935 to account for certain kinetic data which could not be explained in inductive and or polarization terms.[1] The concept of σ-π interaction or hyperconjugation has been extended to many phenomena.[2] A quantum-theoretical study of the subject has been published by Mulliken *et al.*,[3] and very recently by Dewar.[4] Although the carbon-hydrogen bond hyperconjugation has been recognized as a normal effect of the alkyl groups, the existence of carbon-carbon bond hyperconjugation is doubtful, and even if present, it is less significant than carbon-hydrogen bond hyperconjugation.

Based on the analysis of the data on the ionization equilibrium of triphenylmethyl chlorides in sulfur dioxide, Bartlett[5] has shown that "the Baker-Nathan effect is present in both the methyl and the t-butyl" and also that the free energy difference due to carbon-carbon bond hyperconjugation in the latter is about 70% of the former. More recently, Brown *et al.*[6] have calculated the hyperconjugation of alkyl groups from the kinetics of solvolysis of substituted phenyldimethylcarbinyl chlorides. They found that the value for t-butyl was 79% of the methyl. Taft and Lewis,[7] from a number of reported kinetic and equilibrium data, have evaluated the resonance effect of alkyl groups and obtained essentially the same values. The Taft σ_R are: CH_3, $-0{\cdot}102$; C_2H_5, $-0{\cdot}094$; i-C_3H_7, $-0{\cdot}086$; t-C_4H_9, $-0{\cdot}078$.

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* This work was sponsored by the Office of Aerospace Research, United States Air Force, through contract AF 61(052)-141.

[1] J. W. Baker and W. S. Nathan, *J. Chem. Soc.* 1844 (1935).

[2] For a recent survey see: The Conference on Hyperconjugation, *Tetrahedron* **5**, 105–274 (1959).

[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941). See also Ref. 2, p. 253.

[4] M. J. S. Dewar and H. N. Schmeising, Ref. 2, p. 166.

[5] P. D. Bartlett, *J. Chem. Educ.* **30**, 22 (1953); N. N. Lichtin and P. D. Bartlett, *J. Amer. Chem. Soc.* **73**, 5530 (1951).

[6] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bowner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

[7] R. W. Taft and I. C. Lewis, Ref. 2, p. 210.

Spectral evidence for carbon-hydrogen and carbon–carbon bond hyperconjugation has been given on the basis of spectral shifts[8,9] and hyperchromic effects[8] of the alkyl groups. Nevertheless, it is considered that "evidence for hyperconjugation from absorption spectra of alkyl substituted benzene derivatives is not definitive."[10]

Sklar, two decades ago, introduced the concept of migration moment of the substituent in the absorption spectrum of benzene derivatives.[11] This moment is a vector from which the oscillator strength of the secondary band of benzene derivatives (the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition) can be calculated if the substituents and their relative positions in the benzene nucleus are given.

The migration moment, or spectroscopic moment (Platt),[12] depends *exclusively* upon charge migration, into or out from the nucleus, through resonance.[11] * This has further been supported in the case of highly fluorinated benzene derivatives where very strong inductive effects are also present and by the fact that the migration moment is linearly related to the σ_m–σ_p (Hammett) or to the σ_R (Taft) substituent-constant values.[13]

RESULTS

Calculations

It has been shown that the oscillator strength of the secondary band of over 100 polysubstituted benzenes can be calculated within the usual limits of experimental error by vectorial addition of the migration moment of each substituent.[13] This moment is obtained from the oscillator strength of simple benzene derivatives. However, the experimental oscillator strengths are cumbersome to calculate, and in many

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* Coulson [*Proc. Phys. Soc.* **A65**, 933 (1952)] and Longuet-Higgins [*J. Chem. Soc.* 1404 (1952)] have predicted that the induction effect affects little the electronic spectrum of alternant hydrocarbons. This conclusion has been confirmed experimentally in the case of the anilinium ions[11] [see also Doub and Vanderbelt, *J. Amer. Chem. Soc.* **69**, 2714 (1947)] and other aromatic ammonium ions [Peters, *J. Chem. Soc.* 4182 (1957)]. In spite of the extremely powerful inductive effect of the $—NH_3^+$ group the secondary band is located at the same place and has about the same intensity as that of their parent hydrocarbons.

Recently, Petruska [*J. Chem. Phys.*, **34**, 1120 (1961)] from a study of the position and intensity of the secondary band of a number of benzene derivatives has concluded that the migration moment depends exclusively upon the inductive effect. These conclusions concerning this effect upon the $^1B_{2u}$ state cannot be accepted by the present authors because they would mean that (1) fluorine is a strong *electron releasing* substituent but not so powerful as the amino or hydroxy group; (2) the order of electron releasing ability for the alkyl groups is $CH_3 > C_2H_5 > i\text{-}C_3H_7 > t\text{-}C_4H_9$, precisely the opposite of that generally accepted; (3) the inductive effect of $—NH_3^+$ group is the same as that for —H.

These difficulties are removed if, as indicated, it is accepted that the inductive effect plays no role. Accordingly, Murrel has indicated (Theory of the Electronic Spectra of Organic Molecules, Methuen, 1963) that Petruska's results could be explained as well by assuming that the inductive effect of the substituents studied is parallel to their resonance effect. Then the conclusions given in the examples above refer to the resonance effect and are perfectly consistent with the current generally accepted views.

[8] F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Rev.* **41**, 273 (1947).

[9] V. A. Crawford, *J. Chem. Soc.* 2061 (1953).

[10] C. N. R. Rao, *Ultra-violet and Visible Spectroscopy* p. 41. Butterworths, London (1961).

[11] A. L. Sklar, *J. Chem. Phys.* **10**, 135 (1942).

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

[13] M. Ballester, J. Riera, L. Spialter and J. Palav, forthcoming papers.

cases, it is even impossible to obtain accurate values because of the overlap with neighbouring bands. It is, therefore, more convenient to take the maximum absorptivity of the "smoothed" absorption curve $\bar{\varepsilon}$[12] which has been shown to be proportional to the oscillator strength in over 70 carefully selected substances.[13]

When the absorptivities are low, as in most alkyl benzenes, $\bar{\varepsilon}$ can be calculated by Eq. 1

$$\bar{\varepsilon} = \varepsilon_v + (\Sigma_i m_i)^2, \qquad (1)$$

where ε_v is the vibrational term and m_i the migration moment of substituent i. In some cases $\Sigma_i m_i$ vanishes and then $\bar{\varepsilon} = \varepsilon_v$. In benzene $\varepsilon_v = 110$. In substituted benzenes it is believed to vary according to the nature and the number of substituents, being always $\varepsilon_v \geqslant 110$. The vectorial addition is carried out according to rules.[11-13]

In Table 1 the maximum absorptivities $\bar{\varepsilon}$ of some dialkyl benzenes $R_2C_6H_4$ are given. Assuming that the vibrational term is independent of the relative position of the two substituents R, ε_v and m can be easily calculated.

TABLE 1. DIALKYLBENZENES $R_2C_6H_4$

R	$\bar{\varepsilon}_o$	$\bar{\varepsilon}_m$	$\bar{\varepsilon}_p$	m	ε_v
CH_3	234[a]	234[b]	425[c]	8·0	170
C_2H_5	215[d]	212[e]	357[f]	7·0	164
i-C_3H_7	210[g]	214[h]	320[i]	5·9	179
t-C_4H_9	<190[j]	195[k]	274[l]	5·1	169
cyC_6H_{11}	—	—	370[m]	7·1	(170)

[a] A.P.I. Research Project 44, no. 43; [b] no. 44; [c] no. 45; [d] no. 186; [e] no. 187; [f] no. 188; [g] no. 189; [h] no. 190; [i] no. 650; [j] E. M. Arnett and M. E. Strem, *Chem. & Ind.*, 1961, 2008; [k] A.P.I. Project 44, no. 236; [l] no. 750; [m] no. 886.

Since $\bar{\varepsilon}_{meta} = \varepsilon_v + m^2$ and $\bar{\varepsilon}_{para} = \varepsilon_v + (2m)^2$, therefore $m^2 = (\bar{\varepsilon}_{para} - \bar{\varepsilon}_{meta})/3$ and $\varepsilon_v = (4\bar{\varepsilon}_{meta} - \bar{\varepsilon}_{para})/3$.

The m and the ε_v calculated by means of these formulae are given in Table 1. It will be observed that the vibrational term varies little with the nature of the alkyl group, and that, as predicted by theory, the *ortho* and *meta* isomers have similar absorptivity. Since, for the calculation of the migration moment of cyclohexyl in 1,3-biscyclohexylbenzene, no data is available, $\varepsilon_v = 170$ has been assumed.

Adopting the value $m = 8{\cdot}0$ for the methyl group and the average of the ε_v for this and the second alkyl group, the $\bar{\varepsilon}_s$ for the alkyl toluenes listed in Table 2 have been calculated. For p-$RC_6H_4CH_3$ and m-$RC_6H_4CH_3$ the $\bar{\varepsilon}$s are respectively

$$\bar{\varepsilon}_{para} = (170 + \varepsilon_v)/2 + (8{\cdot}0 + m)^2 \qquad (2)$$

$$\bar{\varepsilon}_{meta} = (170 + \varepsilon_v)/2 + (8{\cdot}0 - m)^2 + 8{\cdot}0m \qquad (3)$$

The agreement with the observed values is well within the experimental error, particularly with the *para* isomers. Exceptions are the *o*-n-propyltoluene and the *o*-t-butyltoluene which will be considered later. The ε_vs for the relevant monoalkyl benzenes can be calculated from the moments obtained from the data for $R_2C_6H_4$, the average ε_v value being 128. Based on this value, the $\bar{\varepsilon}$s for the alkyl benzenes listed in Table 3 have been calculated, and the agreement is quite satisfactory.

TABLE 2. ALKYLTOLUENES $RC_6H_4CH_3$

R	$\bar{\varepsilon}_o$		$\bar{\varepsilon}_m$		$\bar{\varepsilon}_p$	
	obs	calc	obs	calc	obs	calc
CH_3	234[a]	(234)	234[b]	(234)	425[c]	(425)
C_2H_5	231[d]	224	231[e]	224	390[f]	392
n-C_3H_7	144[g]	—	235[h]	—	392[i]	—
i-C_3H_7	219[j]	226	220[k]	226	374[l]	369
t-C_4H_9	175[m]	219	216[n]	219	334[o]	342

[a] A.P.I. Research Project 44, no. 43; [b] no. 44; [c] no. 45; [d] no. 63; [e] no. 64; [f] no. 168; [g] no. 745; [h] no. 746; [i] no. 747; [j] no. 534; [k] no. 535; [l] no. 536; [m] no. 520; [n] no. 464; [o] no. 465.

TABLE 3. ALKYL- AND CYCLOALKYLBENZENES

R	$\bar{\varepsilon}$ (obs)	$\bar{\varepsilon}$ (calc)	m
CH_3	192[a]	192	—
C_2H_5	180[b]	177	—
n-C_3H_7	178[c]	—	—
i-C_3H_7	157[d]	163	—
t-C_4H_9	156[e]	154	—
cyC_3H_5	400[f]	—	16·4
cyC_5H_9	210[f]	—	9·0
cyC_6H_{11}	184[f,g]	180	7·1

[a] A.P.I. Research Project 44, no. 42; [b] no. 54; [c] no. 62; [d] no. 160; [e] no. 166; [f] W. W. Robertson, J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5260 (1950); [g] A.P.I. Project 44, no. 652.

DISCUSSION

The vibrational term

The close agreement between the calculated and the experimental values indicates that the vibrational term in the case of the mono- and disubstituted benzenes, is almost independent of the relative positions of the substituents, and also of the nature of the alkyl group. If this is assumed true for all polyalkyl benzenes then the ε_vs listed in Table 4 are valid. As expected, the vibrational term gradually increases with substitution. The ε_v for the tetra-alkylbenzenes given in Table 4 has been calculated from the data for 1,2,3,5-tetramethylbenzene. However, the values obtained for 1,2,4,5-tetra-alkylbenzenes are abnormally high (durene: $\bar{\varepsilon}$, 610; ε_v, 310. 1,2,4,5-tetraisopropylbenzene: $\bar{\varepsilon}$, 530; ε_v, 390).* In this connection it is pointed out that the E_g^+ normal modes of vibration represented in Fig. 1, which are responsible for the existence of the benzene secondary band and, partly, for its vibrational structure,[14] should be influenced in a very particular way by 1,2,4,5-tetra-substitution, since the symmetry of this substitution is clearly related to them. It is therefore, reasonable that this type of substitution enhances the vibrational term.

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* The "expected" $\bar{\varepsilon}_s$ for durene and 1,2,4,5-tetraisopropylbenzene should have been only slightly higher than those for *p*-xylene and *p*-di-isopropylbenzene, respectively, since they have the same resultant migration moment. (Compare with value in Table 1.)

[14] A. L. Sklar, *Rev. Mod. Phys.* **14**, 232 (1942).

TABLE 4. POLYALKYLBENZENES $R_nC_6H_{6-n}$

n	0	1	2	3	4	5	6
ε_v	110	130	170	175[a]	180[b]	195[c]	220[d]

[a] Average of mesitylene, 180 (A.P.I. Project 44, no. 164), hemimellitene, 170 (idem no. 162), 1,3,5-tri-t-butylbenzene, 170 (idem no. 622), and 1,3,5-tri-i-propylbenzene, 180 (idem no. 620).

[b] From 1,2,3,5-tetramethylbenzene, 245 (A.P.I. Project 44, no. 44).

[c] From pentamethylbenzene, 260 (A.P.I. Project 44, no. 393).

[d] Average of hexamethylbenzene, 225 (M.C.A. Project, no. 36), and hexaethylbenzene, 215 (A.P.I. Project 44, no. 488).

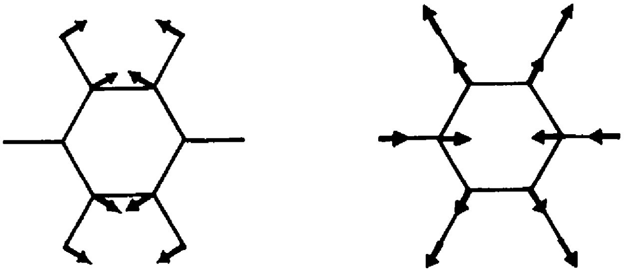

FIG. 1

Such vibrational abnormality should apparently take place in penta- and hexa-homosubstituted benzenes also, since these are "loaded" in the 1,2,4 and 5 positions. Nevertheless, the values found (Table 4) are not abnormally high. This fact is in the authors opinion particularly enlightening since it shows that interaction between electronic migration due to the substituents and vibrational and/or static distortion is the cause for the transition-moment exaltation observed in the 1,2,4,5-tetra-alkyl substituted benzenes. In the penta- and hexa-alkyl-substituted benzenes, where the theoretical resultant migration moments are, as compared with that of durene, low and zero, respectively, the interaction must be practically absent and hence the moment exaltation.

The *apparent* vibrational term for 1,2,4,5-tetra-t-butyl-benzene should not differ significantly from that of 1,2,4,5-tetraisopropylbenzene. Yet, it is considerably lower, not too far from normal ($\bar{\varepsilon}$, 360; ε_v, 250). In this connection, it is pointed out that the former substance is sterically strained. That such strain affects the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition is shown by the lack of fine structure of the secondary band. It is reasonable to assume therefore that steric compression between the bulky t-butyl groups hinders considerably the vibrations of Fig. 1, the vibrational perturbation being diminished accordingly.

This assumption is further confirmed by the absorptivities of the secondary band of *o*-t-butyltoluene, *o*-di-t-butylbenzene and *o*-dibromobenzene,[13] which absorb considerably less than their *meta* isomers in spite of having the same resultant migration moment (Tables 1 and 2).

The Baker-Nathan effect

It has been shown[12,13] that the migration moment of the methyl group is positive. Consequently, through resonance, all alkyl groups are electron-releasing substituents. The data reported in Table 1 shows that the migration moment diminishes about one unit per hydrogen replaced by methyl. The value for the t-butyl group, which is a measure of the carbon-carbon bond hyperconjugation, is 65% that of the methyl group, due to carbon-hydrogen hyperconjugation.* This value is consistent with those obtained from equilibrium and kinetic data mentioned in the Introduction. The parallelism between the migration moment and the σ_R values[13] is also found here.

TABLE 5. n-RC_6H_5 (ε_v, 128)

n-R	$\bar{\varepsilon}$	m
CH_3	192[a]	8·0
C_2H_5	182[a]	7·0
C_3H_7	178[a]	7·1
C_4H_9	189[b]	7·8
$C_{10}H_{21}$	189[c]	7·8

[a] See Table 3;
[b] A.P.I. Research Project 44, no. 176;
[c] no. 571.

TABLE 6. C_6H_5-$(CH_2)_n$-C_6H_5 (ε_v, 128)

n	$\bar{\varepsilon}$	m
1	411[a]	8·8
2	368[b]	7·5
3	366[c]	7·4
4	414[d]	8·9
6	372[e]	7·6

[a] A.P.I. Research Project 44, no. 821; [b] no. 823; [c] no. 829; [d] no. 798; [e] no. 806.

It is seen in Tables 2, 3 and 5 that the contribution of the n-alkyl groups to the absorption is about the same as that for the ethyl group, in agreement with the fact that the contributing hyperconjugating bonds are also the same. It may, however, be noticed that in the n-alkylbenzenes (Table 5) the moment of the substituent approach that of the methyl group as the size of the substituent increases (Table 6). This might be traced to a minor increase of the vibrational term.

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* The hyperconjugation the authors are here referring to is that taking place with a net charge migration. The preceding studies on hyperconjugation here quoted concern the relevant effect upon functions involving pairs of states (equilibrium: initial and final state; kinetics: ground and transition state; spectral shifts: ground and excited state). The effect dealt with here is that upon the transition moment, a function of the ground and excited state.

We are indebted to a referee of the present paper for suggesting the necessity of this explanatory note.

Static distortion effects

In a forthcoming paper[13] it will be shown that out-of-plane distortion due to steric repulsions enhances the value of the migration moment of the substituents. It has also been found that when distortion is great important bathochromic shifts take place and the vibrational structure disappears.[15]

In connection with the effects of static distortion due to ring-strain, spectral studies on the secondary band of benzocycloalkenes have been reported recently by Marcus,[16] and Rapoport.[17] From their graphical data, the $\bar{\varepsilon}$s have been calculated and are listed in Table 7. Ring strain and absorptivity increases from I to VIII (Table 7).

A priori, two major effects are present: bond-bending in the aliphatic ring and distortion of the benzene nucleus. That distortion within the substituent enhances its migration moment is apparent from the data included in Table 3 on cycloalkyl benzenes, where no benzene-ring distortion is involved.* Fusion with the benzene ring increases the strain further and consequently it might be expected that the relevant moments would be even higher. On the other hand, as it has been indicated before, ring-distortion also gives rise to moment exaltation in cases where ring-substituent strain is absent. It is, therefore, reasonable to assume that both effects are in operation, making it impossible to deal with them separately. It should be understood that the migration moments which are going to be mentioned include both effects, and are consequently a measure of the overall perturbation of symmetry. It is assumed that benzene-ring distortion in benzocycloalkenes is mostly in-plane. Although the greatest distortion is found in benzocyclobutene, there is neither significant loss of fine structure nor bathochromic shift of the secondary band. This is a striking difference from the out-of-plane distortion. It will be noticed that benzocyclooctene has a somewhat high absorptivity (or resultant migration moment). This is attributed to some distortion due to overcrowding of methylene groups.

The migration moments listed in Table 7 have been calculated using the vibrational terms of Table 4 and Eq. 1.

From the moments of IV and VI in Table 7, assuming that the distortional effects of the two cycloalkene rings do not interact and that Eq. 1 is still applicable, the $\bar{\varepsilon}$s of IX and X have been calculated (the moments should be twice as high). It will be seen in Table 7 that the agreement with the observed values is excellent. The values for XI, XII, XIII and XIV cannot be calculated as simply as before since obviously the distortions due to each ring-substituent must interact strongly.

In the process of building up XI from VI at least an additional strain is created on the carbon 2 because of the second ring, and conversely, more strain occurs on carbon 3 than it would in the absence of the original ring. This will increase the contribution of the substituents on 2 and 3 and consequently the resultant migration

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* This effect is probably caused by increased carbon-carbon bond hyperconjugation due to bond bending.

[15] M. Ballester and J. Castañer, *J. Amer. Chem. Soc.* **82,** 4259 (1960); M. Ballester, J. Castañer and E. Guardiola, *Anales real soc. españ. fís. y quím.* **56B,** 723 (1960).

[16] E. Marcus, W. M. Lauer and R. T. Arnold, *J. Amer. Chem. Soc.* **80,** 3742 (1958); W. R. Moore, E. Marcus, S. E. Fenton and R. T. Arnold, *Tetrahedron* **5,** 179 (1959).

[17] H. Rapoport and J. Z. Pasky, *J. Amer. Chem. Soc.* **78,** 3788 (1956); H. Rapoport and G. Smolinsky, *Ibid.* **82,** 1171 (1960).

Table 7. Bond strained benzenes

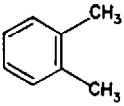
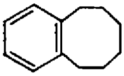
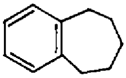
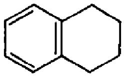
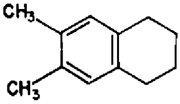
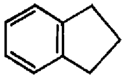
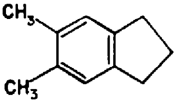
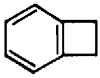
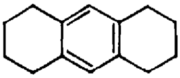
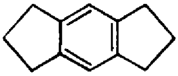
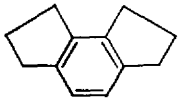
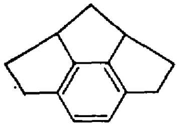
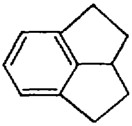
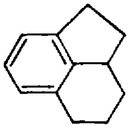
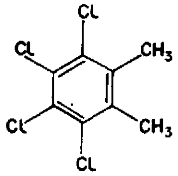
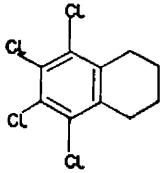
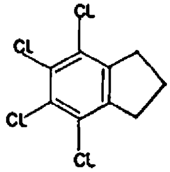
Compound		$\bar{\varepsilon}$(obs)	$\bar{\varepsilon}$(calc)	m
I		234^{a}	—	8·0
II		280^{b}	—	10·5
III		230^{b}	—	7·8
IV		465^{b}	—	17·2
V		950^{b}	960*	—
VI		1040^{b}	—	29·5
VII		1900^{b}	1800*	—
VIII		$\sim 1300^{b}$	—	~33·6
IX		1450^{b}	1360	—
X		3700^{b}	3660	—

Table 7 (*contd.*)

	Compound	$\bar{\varepsilon}$(obs)	$\bar{\varepsilon}$(calc)	*m*
XI		700[c]	<1040	—
XII		470[c]	<700	—
XIII		640[c]	635	—
XIV		670[c]	<840	—
XV		235	240[e]	—
XVI		270	240	—
XVII		450	480	—

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[a] A.P.I. Research Project 44, no. 43; [b] reference 16; [c] reference 17.

[e] Assuming that *m* for methyl is 10·8, as in durene.[18]

moment (or transition moment) will be less than the calculated value. As the resultant moment of VI and XI would otherwise be equal, it is concluded that the absorptivity of the latter will be smaller than that of the former, as observed.

In XII the distortions operating on carbons 1, 2, 3 and 4 are much larger. If the effects on carbons 2 and 3 are much greater than those on carbons 1 and 4 (the closer the perturbation site the bigger the effect), the absorptivity of XII should be, as observed, significantly smaller than that of XI. Of the compounds listed in Table 7, XII is by far the most out-of-plane distorted. Accordingly, the secondary band appears shifted bathochromically about 17 mμ from the normal location and the vibrational structure is lost.

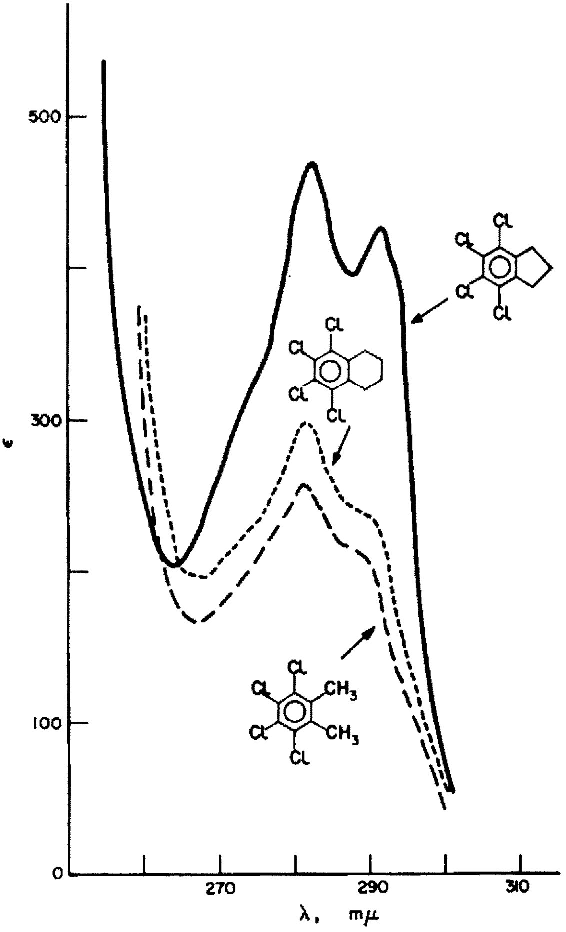

Fig. 2

Bond with carbon 2 in XIII should not be in-plane bent. Assuming that the system is about planar* the migration moment for the methylene on carbon 2 should be normal (~8·0). Those of the methylenes on carbons 1 and 3 can be taken as in VI (29·5). The calculated $\bar{\varepsilon}$ is precisely the observed value.

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* There is no significant loss of the fine structure of the secondary band.

An upper limit for the absorptivity of XIV is calculated by assuming that the moments of the substituents on carbons 1 and 2 have the same values as in VI, and that carbon 3 is somewhat more strained than carbon 1 or 2 in IV. These assumptions lead to $\bar{\varepsilon} < 840$, which is consistent with the observed value.

The absorptivities of substances V and VII are calculated as usual from the moments obtained from IV and VI. The agreement is very good.

In Table 7 and Fig. 2, data concerning some relevant highly chlorinated derivatives prepared in this laboratory have been included.* The calculated values have been obtained by assuming that the moment for chlorine is 14·0 (as in any 1,2,3-trichlorobenzene[13]) and that the vibrational term is 230.[13] The value for XVI is too low. This might be caused by additional distortion due to the greater steric interaction between the aliphatic ring and the vicinal chlorines.

As far as is known, the highest absorptivity (or oscillator strength) for the secondary band of a benzene derivative ever reported is that of X. It has been shown that in other than in-plane distorted benzenes there is a saturation effect that makes Eq. 1 quite useless for high resultant migration moments.[13] Apparently, such effect is unimportant in in-plane distorted benzenes. It may be noted in this connection that X is a 1,2,4,5-tetra-alkylbenzene.

Acknowledgements—The authors wish to acknowledge their appreciation to Professor José M. Codina, Dr. Juan Castañer, Mr. José Masclans and Miss Julia Simón for their valuable assistance and discussions.

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* The spectra were taken in benzene-free *cyclo*hexane by means of a Hilger *Uvispek* ultraviolet and visible spectrophotometer.