420. *Hyperconjugation. Part III.* Bathochromic Shifts resulting from Methyl Substitution in Conjugated Systems.*

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A molecular-orbital calculation of the frequency of absorption of methyl-substituted ethylenes and benzenes has been made and the results compared with experiment. In agreement with Mulliken it is concluded that the red shifts in the spectra result chiefly from hyperconjugation.

It is well known (Askew, *J.*, 1935, 509; Mohler, *Helv. Chim. Acta*, 1937, **20**, 811; Gillam, *J.*, 1940, 543; Billroth, *Z. physikal. Chem.*, 1936, **33**, *B*, 133; Forster and Wagner, *ibid.*, 1937, **35**, 343) that replacement of the hydrogen atoms of ethylene or aromatic hydrocarbons by alkyl groups results in spectra which are similar in shape to that of the unsubstituted hydrocarbon, but the whole absorption curve is shifted to longer wave-lengths. Shift of the spectrum to longer wave-lengths implies a decrease in the energy-level differences between the ground and excited states. This may result either from a raising of the ground state level, a lowering of the levels of the excited states, or a combination of the two. The reasons for these changes are not as yet completely clear. Thus it has been suggested (Mulliken, *J. Chem. Phys.*, 1939, **7**, 339; *Rev. Mod. Phys.*, 1942, **14**, 265) that the small increase in the resonance stabilisation energy of the alkyl derivatives resulting from hyperconjugation is of the correct order of magnitude to account for the observed spectral shifts. On the other hand (Walsh, *Ann. Reports*, 1947, **44**, 32; *Quart. Reviews*, 1948, **2**, 73) the appearance of the bathochromic shift has been attributed to reduction in ionisation potential of the ethylenic or aromatic centre by " charge transfer " through an inductive mechanism from the alkyl groups. Now charge transfer, or migration of charge, can arise not

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* Part II, preceding paper.

only from the inductive effect but also from conjugation and hyperconjugation. Since both types of effect must occur, the present work was undertaken as part of a programme the object of which was to determine the relative importance of the two effects.

Method of Calculation.—In order to explain in detail the more quantitative aspects of spectra, antisymmetrisation is necessary, *i.e.*, the molecular " eigenfunction " of the ground state and the excited state must be multiplied by an appropriate spin function and made completely antisymmetrical with respect to exchange of electrons. The added complication of antisymmetrisation will not be used here, however, for straightforward calculations by the simple LCAO molecular-orbital method have been quite successful in explaining the electronic structure and ultra-violet spectra of molecules. Indeed it has recently been emphasised (Platt, *J. Chem. Phys.*, 1950, **18**, 1168) how accurate can be the simple calculations of the π-electronic spectra of conjugated systems. The numerical values assigned to the parameters were the same as those used in Part I and the computations reported here refer to the hyperconjugative effect only.

Since on excitation the electron spins may be parallel or antiparallel, our simple procedure really predicts the centre of gravity of singlet–triplet pairs for nondegenerate cases, whereas for degenerate cases it predicts the centre of gravity of a whole set of singlets and triplets, *i.e.*, of a configuration. If the approximate singlet–triplet separation ε is known, $\varepsilon/2$ may be added to the prediction to locate the singlet more accurately; or subtracted to locate the triplet. In general, however, this correction cannot be made for it is known in only a few cases.

Substituted ethylenes. Propylene, *cis*-butene, *iso*butene, and 2 : 3-dimethylbut-2-ene (tetramethylethylene) belong respectively to the symmetry groups, C_{1h}, C_{2v}, C_{2v}, D_{2h}.

In the ground state of the molecules the mobile electrons occupy in pairs all the bonding orbitals, the ground state descriptions being as in Table 1, electrons of greatest binding energy being given first.

TABLE 1.

Molecule	Configuration	Ground state
Propylene	$(a'')^2(a'')^2$	A'
cis-Butene	$(b_1)^2(a_2)^2(b_1)^2$	A_1
*iso*Butene	$(b_1)^2(a_2)^2(b_1)^2$	A_1
2 : 3-Dimethylbut-2-ene	$(b_{3u})^2(b_{1g})^2(b_{2g})^2(a_{1u})^2(b_{3u})^2$	A_{1g}

Different excited states are obtained by taking an electron from a bonding orbital and placing it in an anti-bonding one. The first excited state corresponds to the transition from the highest bonding orbital (N) to the lowest anti-bonding one (V_1). The corresponding transition is designated N $\longrightarrow V_1$ and the corresponding excitation energy determines the longest wave-length absorption. Table 2 shows the first excited states, the direction of polarisation being longitudinal.

TABLE 2.

Molecule	Upper state	Absorption process
Propylene	$(a'')(a'')$	$A' \longrightarrow A'$
cis-Butene	$(b_1)(a_2)$	$A_1 \longrightarrow B_2$
*iso*Butene	$(b_1)(b_1)$	$A_1 \longrightarrow A_1$
2 : 3-Dimethylbut-2-ene	$(b_{3u})(b_{1g})$	$A_{1g} \longrightarrow B_{2u}$

The computed energy values corresponding to the $N \longrightarrow V_1$ transition for the methylated ethylenes as well as the observed values are presented in Table 3. Since, as mentioned previously, singlet and triplet levels arise on excitation, the singlet may be more accurately located by adding to the computed excitation energy a quantity $\varepsilon/2$ corresponding to half the singlet–triplet separation.

The experimental values are taken from Mulliken (*Rev. Mod. Physics*, 1942, **14**, 265) who points out that the $N \longrightarrow V$ data refer to $\nu_{\text{max.}}$. In combining them with the N-term values given an estimated correction of 0·2 has been added to reduce them to $\nu_{\text{max.}}$ values (vertical excitation potentials).

Ionisation potentials. The experimental data show that there is a linear relation between the values for the ground and excited state terms and the number of methyl groups in a methylated ethylene. However, the initial drop in the N-term value on passing from ethylene to propylene seems to be somewhat greater than that resulting from the further methylation of ethylene. The theoretically computed shifts in term values on the other hand are almost strictly proportional to the number of substituent methyl groups.

TABLE 3. *Term values and spectra of methyl-substituted ethylenes.*

	Experimental			Computed			
	N, ev	V_1, ev	$N \longrightarrow V_1$, ev	N	V_1	$N \longrightarrow V_1$	ev
Ethylene	10·45	3·04	7·61	$\alpha_0 + 0{\cdot}8504\beta_0$	$\alpha_0 - 1{\cdot}4794\beta_0$	$2{\cdot}3298\beta_0$	7·61
Propylene	9·6	2·66	7·14	$\alpha_1 + 0{\cdot}7964\beta_0$	$\alpha_1 - 1{\cdot}4246\beta_0$	$2{\cdot}2210\beta_0$	7·25
cis-Butene	9·2	2·38	7·02	$\alpha_2 + 0{\cdot}7470\beta_0$	$\alpha_2 - 1{\cdot}3751\beta_0$	$2{\cdot}1221\beta_0$	6·93
*iso*Butene	—	—	—	$\alpha'_2 + 0{\cdot}7537\beta_0$	$\alpha'_2 - 1{\cdot}3776\beta_0$	$2{\cdot}1313\beta_0$	6·96
2 : 3-Dimethylbut-2-ene	8·3	1·72	6·78	$\alpha_4 + 0{\cdot}6684\beta_0$	$\alpha_4 - 1{\cdot}2930\beta_0$	$1{\cdot}9614\beta_0$	6·40

The computed result recorded in Table 3 show that the hyperconjugative effect raises the ground-state and lowers the excited-state energies. On the other hand, preliminary calculations (*e.g.*, Coulson, " Valence," Oxford Univ. Press, 1952, p. 309) show that the inductive effect raises both the ground-state and the excited-state energies. This co-operation of the two effects on the ground state results in slightly greater shift in N-term values as compared with the V-term values. Because the magnitude of the inductive effect on the excited state is greater than that of the hyperconjugative effect, this results in an overall decrease in experimental V-term values. Since, however, the two effects act in opposition on the excited state, the shifts in V-term values with progressive methylation is smaller than that produced in the ground state.

Theoretical calculation gives the N- and V-term values but only within the additive quantity α which is usually supposed to be constant, at least for a given molecule. If α were the same for different methylated compounds the computations would give directly the changes in N- and V-term values on methyl substitution. Comparison of the computed and experimental ionisation potentials shows that the latter decrease much more rapidly than the former, indicating that $-\alpha$ decreases with methyl substitution. Now it has been shown (Mulliken, *Phys. Review*, 1948, **74**, 76) that, other things being equal, $|\alpha|$ decreases in magnitude with an increase in the number of atoms covered by the molecular orbital. Thus for example there is a progressive decrease in ionisation potential on passing from ethylene through butadiene to benzene. Since hyperconjugation implies that the methyl group may be regarded as part of the conjugated system, a portion of the decrease must result from merely increasing the number of atoms in the conjugated system. Nevertheless, in agreement with that of Mulliken (*Rev. Mod. Physics*, 1942, **14**, 265) the present work indicates that about 0·2 ev of the observed decrease in ionisation potential is attributable to hyperconjugation.

Frequencies. Comparison of the observed and computed excitation energy for ethylene gives a value for β_0 of $-3{\cdot}27$ ev. This value is then used to convert the computed $N \longrightarrow V$ data into ev. It is at once apparent that the computed frequency shifts are of the right order of magnitude and that they are proportional to the number of methyl groups. The experimental shifts are roughly proportional to the number of substituent methyl groups although the initial drop in excitation energy on passing from ethylene to propylene is slightly greater than that resulting from further substitution.

Recently Coulson (*Proc. Phys. Soc.*, 1952, **65**, *A*, 933) examined in a general theoretical manner the shifts in the spectrum resulting from alkyl substitution in hydrocarbons. The influences of the inductive and hyperconjugative effects on the spectral properties are quite distinct, the change in energy from the inductive effect being given by $2ASc_{r1}{}^2\delta\alpha_r$, where A is a positive constant, S the overlap integral, c_{r1} the coefficient c_r for orbital 1 and $\delta\alpha_r$ the change in the coulomb term of the carbon atom to which the methyl group is attached. Since $\delta\alpha_r$ is positive for methyl the above expression shows that the energy shifts resulting from the operation of the inductive effect wlll always be positive, leading to hypsochromic shifts. On the other hand the hyperconjugative effect on alternant hydrocarbons is always bathochromic. Since here an overall red shift occurs, the red shift due to hyperconjugation must be of larger magnitude than the inductive effect.

From Table 3 it is seen that *iso*butene is predicted to have a slightly greater wave number than *cis*-butene. This is in complete accord with Carr and Stücklen's experimental results (*J. Chem. Phys.*, 1936, **4**, 760) which showed that $CHR{=}CHR$ has on average a slightly lower wave number for the first band than $CR_2{=}CH_2$.

Methylbenzenes. The ground state descriptions of these molecules are given in Table 4.

TABLE 4.

	Molecule	Description	Ground state
C_{2v}	Toluene	$(b_1)^2(b_1)^2(a_2)^2(b_1)^2$	A_1
C_{2v}	*o*-Xylene	$(b_1)^2(a_2)^2(b_1)^2(a_2)^2(b_1)^2$	A_1
C_{2v}	*m*-Xylene	$(b_1)^2(a_2)^2(b_1)^2(b_1)^2(a_2)^2$	A_1
D_{2h}	*p*-Xylene	$(b_{3u})^2(b_{1g})^2(b_{3u})^2(b_{2g})^2(b_{1g})^2$	A_{1g}
D_{3h}	Mesitylene	$(a'')^2\underbrace{(e'')^2(e'')^2}(a'')^2\underbrace{(e'')^2(e'')^2}$	A_1
D_{2h}	Durene	$(b_{3u})^2(b_{2g})^2(b_{1g})^2(a_{1u})^2(b_{3u})^2(b_{1g})^2(b_{2g})^2$	A_{1g}

The substituent reduces the symmetry of benzene, resulting in a splitting of the degenerate benzene levels; two close lying states arise, the transition energies for which are recorded in Table 5.

In order to calculate the wave-length and intensity of the near ultra-violet absorption of a substituted benzene, the nature of the transition must be established. In benzene the excitation of an electron from the highest filled orbital to the lowest unoccupied orbital would produce an excited singlet and triplet state each with four-fold degeneracy. When electron repulsion is included the degeneracy is removed and there results a group of three singlet and three triplet states. The energies of excitation as calculated here without electron repulsion give the average height of the actual states. A value for β_0 is deduced by identifying the 2600λ band with the computed transition energy of $2{\cdot}1333\beta_0$. This value of β_0 is then combined with the *average* excitation energy to yield the computed frequencies recorded below.

TABLE 5.

Molecule	Upper state	Absorption process	Polarisation	Excitation energy
Toluene	$(b_1)(b_1)$	$A_1 \longrightarrow A_1$	z	$2{\cdot}0671\beta_0$
	$(b_1)(a_2)$	$A_1 \longrightarrow B_2$	y	$2{\cdot}0976\beta_0$
o-Xylene	$(b_1)(a_2)$	$A_1 \longrightarrow B_2$	y	$2{\cdot}0334\beta_0$
	$(b_1)(b_1)$	$A_1 \longrightarrow A_1$	z	$2{\cdot}0636\beta_0$
m-Xylene	$(a_2)(a_2)$	$A_1 \longrightarrow A_1$	z	$2{\cdot}0382\beta_0$
	$(a_2)(b_1)$	$A_1 \longrightarrow B_2$	y	$2{\cdot}0669\beta_0$
p-Xylene	$(b_{1g})(b_{1g})$	$A_{1g} \longrightarrow A_{1g}$	forbidden	$2{\cdot}0075\beta_0$
	$(b_{1g})(b_{3u})$	$A_{1g} \longrightarrow B_{2u}$	y	$2{\cdot}0075\beta_0$
Durene	$(b_{2g})(b_{3u})$	$A_{1g} \longrightarrow B_{1u}$	z	$2{\cdot}0054\beta_0$
	$(b_{2g})(a_{1u})$	$A_{1g} \longrightarrow B_{2u}$	y	$1{\cdot}9507\beta_0$

The yz plane has been taken to correspond to the plane of the molecule. In toluene, *o*-xylene, and *m*-xylene the z-axis is the symmetry axis whereas in *p*-xylene and durene the z-axis has been taken to be the shorter dimension of the molecule.

Molecule	Toluene	*o*-Xylene	*m*-Xylene	*p*-Xylene	Benzene
Exptl. λ, Å	2668	2709	2724	2745	2610
Calc. λ, Å	2674	2717	2711	2773	2610
Computed transition energy	$2{\cdot}0823\beta_0$	$2{\cdot}0485\beta_0$	$2{\cdot}0526\beta_0$	$2{\cdot}0075\beta_0$	$2{\cdot}1333\beta_0$

Just as in the case of the methylated ethylenes so here too the computed frequency shifts are of the right order of magnitude. Unfortunately, experiment shows that *o*-xylene suffers the least displacement whereas theory predicts this for *m*-xylene; but the difference is not large. However, in accordance with experiment, theory predicts that of the three xylenes the *para*-isomer experiences the greatest displacement.

It has already been pointed out that the inductive effect alone would result in spectra being displaced to shorter wave-lengths. Since, however, an overall displacement to the visible occurs and since the computed N, V frequency shifts are in fair agreement in both magnitude and direction with experiment, it may be taken that the shifts towards the red are due chiefly to hyperconjugation and not to charge transfer or inductive effects. However, there is evidence (Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5252) that in certain molecules the inductive effect might be of the same magnitude as the resonance effect. Results of calculations based solely on the inductive effect will be reported later but in the meantime the following considerations may be noted.

The NH_3^+ group, which certainly promotes a strong inductive effect but is incapable of large-scale participation in a resonance effect, brings about no significant change in the spectrum of benzene. The NO_2 group on the other hand, which like the amine cation is also highly *meta*-directing, is one of the most effective displacing groups. An important point of contrast between these groups is the difference in their ability to participate in actual electron transfer. This would seem to imply that the effects which cause displacement of the bands are similar to, if not identical with, the conjugative as contrasted with the inductive effect.

Furthermore, attention is directed to the fact that in toluene and chlorobenzene two groups as unlike as methyl and chloro behave as auxochromes to the same extent. With chlorine the inductive effect would oppose the contribution of negative charge to the ring. On the other hand, the chlorine atom has electron pairs which may conjugate with the ring π electrons and this latter effect predominates to produce a net auxochromic effect.

This conclusion that where the inductive and conjugative effects occur simultaneously the latter predominates is reinforced by a consideration of the spectroscopy of the chloroethylenes. The inductive effect is usually regarded as being of short range and is therefore likely to be of greater importance in small molecules than large. Yet in the chloroethylenes the electronic levels and ionisation potentials as a whole are shifted to long wave-lengths (Walsh, *Trans. Faraday Soc.*, 1945, **41**, 35). The large electronegativity of the chlorine atom would lead one to expect the opposite on a simple inductive-effect basis. The experimentally observed effect must therefore be due to conjugation between the electrons of the double bond and the lone pair of the chlorine atom. Furthermore, as the number of chlorine atoms is increased the increasing conjugation of the π electrons of the double bond with the $p\pi$ electrons of chlorine displaces the transition more and more to long wave-lengths. So, for example, in the dichloro-compound the C=C bond is subjected to twice as great an inductive effect as in vinyl chloride, yet despite this the first maximum occurs at longer wave-lengths.

This conclusion that the bathochromic frequency shifts are due to a delocalisation rather than to an inductive effect has recently been established on a semi-quantitative basis by Daub and Vandenbelt (*J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414), who correlated the displacement of the primary band with the direction and extent of resonance interaction between the substituent groups of *para*-disubstituted benzene derivatives. The available evidence therefore seems to support Bateman and Koch's contention (*J.*, 1944, 600) that double-bond absorption is very much less sensitive to inductive influences than has hitherto been supposed.

The results reported here have been obtained by use of the simple LCAO treatment, including overlap, but excluding antisymmetrisation and allowance for configurational interaction. This interaction changes the energies and wave-function of two neighbouring states which have the same symmetry. Such states mix so that the lower state has its energy lowered further and the upper state has its energy raised, the effects being more marked the closer the two states are together. This effect is particularly important in the case of excited states for frequently the energy differences between excited states are to a large extent due to electron interaction. Coulson, Craig, and Jacobs (*Proc. Roy. Soc.*, *A*, 1950, **202**, 498; 1951, **206**, 287) have demonstrated its importance although for a comparative study its omission is probably not too serious.

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