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ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—V*

EFFECT OF TERMINAL GROUPS CONTAINING MULTIPLE BONDS ON THE K-BANDS OF CONJUGATED SYSTEMS

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Abstract—The investigation of the effect of terminal groups of absorbing (conjugated) systems on the corresponding K-bands is extended to groups containing multiple bonds. A consistent theoretical interpretation of all observations is given based on the consideration of the electronic perturbations in the excited state (due to Heisenberg resonance) and the view that organic molecules are built up of localised bonds and involve inductive electron-shifts only. The empirical comparative analysis of the experimental data shows conclusively that, in contrast to the conclusions arrived at by mathematical methods, the 2000 Å, and not the 1800 Å, band system of benzene corresponds to an excited state of the (approximate) symmetry ${}^1E_{1u}$ (involving an allowed transition characteristic for all K-bands).

INTRODUCTION

An earlier analysis of numerous properties of organic molecules has led to the conclusion that these molecules are built up of localised bonds (orbitals) and that the constitutive changes of these bonds are due to modifications of effective nuclear charges and involve inductive electron displacements only.[1] More recently[2] it has been shown that on this basis a qualitative, but very detailed understanding of all observations related to the electronic spectra of organic molecules becomes possible, if the electronic perturbations in *excited* states (due to wave-mechanical resonance in Heisenberg's original sense) are considered.

Evidence has been given[3–6] that the electron migration in one direction along an absorbing (conjugated) system (the "effective" electron migration) determines the stability of the excited state corresponding to a K-band. This state can be represented as a "hybrid" of interacting unperturbed excited states each involving one excited electron.

It has been suggested[2] to express this, for convenience, by one simplifying formula only such as (I), in which each arrow corresponds to the excited electron of one unperturbed excited state and also indicates the direction of the electron migration

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* Part IV, *Tetrahedron* 4, 403 (1958).

[1] A. Burawoy, *Contribution to the Study of Molecular Structure* p. 73. Desoer, Liège (1947–48); *Trans. Faraday Soc.* 40, 537 (1944); *Disc. Faraday Soc.* 10, 104 (1951); *Chem. & Ind.* 63, 434 (1944); *J. Chem. Soc.* 3752 (1954).

[2] A. Burawoy, *Tetrahedron* 2, 122 (1958).

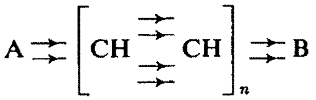
[3] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2085 (1955).

[4] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2557 (1955).

[5] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).

[6] A. Burawoy, J. P. Critchley and A. R. Thompson, *Tetrahedron* 4, 403 (1958).

(on one side of the nodal plane formed) in phase with the effective charge migration of the observed transition. (There is, of course, no intention to attach any importance to the formulation itself.)



$$A \rightrightarrows \left[\mathrm{CH} \overset{\rightrightarrows}{\underset{\rightrightarrows}{}} \mathrm{CH}\right]_n \rightrightarrows B \qquad \mathrm{I}$$

A K-band is displaced to longer wavelengths by any structural modification which increases the polarisability of the electrons in the absorbing system, i.e. the stability (of the part-orbitals in phase with the effective electron migration) of the corresponding unperturbed excited states. This may be due either to an *electron-shift* in the ground state coinciding with the direction of the effective charge migration of the transition, which may be caused e.g. by a change of a terminal group or of the solvent, or to a *replacement* of a bond or group (electronic unit) by a more strongly polarisable one.

The discussion of the effect of terminal methyl groups,[3] substituted methyl groups[4] and atoms with lone electron pairs[5,6] of absorbing systems such as (I) on the position of the corresponding K-bands is now extended to the effect of terminal groups containing multiple bonds (I, A or B: $CH{=}CH_2$, $CH{=}NMe$, $CH{=}O$, $NO{=}O$, $C{\equiv}CH$, $C{\equiv}N$).

MONOSUBSTITUTED BENZENE DERIVATIVES

Data for the maxima and intensities of the K-bands of benzene, styrene, N-methylbenzaldimide, benzaldehyde, nitrobenzene, phenylacetylene and phenylcyanide in hexane and ethanol solution, as well as the displacements (D) of the benzene K-band (appearing at 2020–2030 Å in various solvents) on introduction of the substituents, are shown in Table 1. The effective electron migration of the transition corresponding to the K-band (observed at longest wavelengths) of these compounds is towards the substituent as indicated by a long arrow in (II).

$$\xrightarrow{C_6H_5-X} \quad (X : CH{=}CH_2,\ CH{=}NMe,\ CH{=}O,\ NO{=}O,\ C{\equiv}CH,\ C{\equiv}N) \qquad \mathrm{II}$$

(a) *Styrene*, N-*methylbenzaldimide*, *benzaldehyde*, *nitrobenzene*

The displacements to longer wavelengths of the K-band of benzene in hexane solution (~2020 Å) decrease in the order of substituents $CH{=}CH_2$ (D, 430 Å) $>$ $CH{=}NMe$ (D, 398 Å) $>$ $CH{=}O$ (D, 388 Å), although the polarity and electron-attracting power of these groups increases in the given order. In these simple compounds, the moderate bathochromic effect to be expected from the electron-shifts in the substituted phenyl group (on introduction of the electron-attracting $CH{=}NMe$ and $CH{=}O$ groups) is completely masked by the effect of the electron polarisability increasing in the reversed order $-CH{=}O < -CH{=}NMe < -CH{=}CH_2$.*

However, in more polar solvents and on substitution of other systems (cf. below) the relative importance of these two factors as well as the order of the polarisability of these groups may undergo appreciable changes. Thus, solvent-solute interactions on replacement of hexane by the more polar ethanol as solvent are responsible (in the ground state) for electron-shifts within the absorbing systems. These shifts are

* Similarly, 1-methylbutadiene absorbs in hexane at longer wavelengths (λ, 2240 Å; ε, 26·000)[7] than crotonaldehyde (λ, 2190 Å; ε, 9300).

[7] K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.* 948 (1946).

negligible in the only slightly polar styrene, appreciable in the more polar N-methylbenzaldimide and highest in benzaldehyde and result in increasing displacements of the K-bands in the given order. Their positions are now almost identical for all three substances (2453, 2450 and 2445 Å respectively).

This effect is even greater on addition of a proton to N-methylbenzaldimide and benzaldehyde respectively, e.g. on salt formation in concentrated sulphuric acid. The increased polarity (and, thus, electron polarisability) of the absorbing system in the ions (III) results in an appreciable displacement of the K-bands to longer wavelengths. The K-band of the conjugate acid of benzaldehyde appears at longer wavelengths (λ, 2950 Å; ε, 26·000) than that of the conjugate acid of N-methylbenzaldimide (λ, 2810 Å; ε, 20·000), because the electron-attracting power and, probably, the electron polarisability of the $C{=}\overset{+}{O}H$ group are greater than those of the $C{=}\overset{+}{N}HMe$ group. (For the greater bathochromic effect of a charged $=\overset{+}{O}H$ group as compared with a charged $=\overset{+}{N}H_2$ group in cations and for the significance of this observation, cf. also Burawoy.)[8]

$$\underrightarrow{C_6H_5{-}CH{=}\overset{+}{O}H}\ (=\overset{+}{N}HMe) \qquad \text{III}$$

The K-band of nitrobenzene appears at 2513 Å in hexane and at 2595 Å in ethanol. The effect of the nitro group is similar to that of the formyl group, but the nitro group is more strongly electron-attracting and (mainly for this reason) is responsible for a greater displacement of the benzene K-band (D, 493 Å in hexane and 565 Å in ethanol). In agreement with this interpretation the displacement of the K-band of nitrobenzene on replacing hexane by the more polar ethanol as solvent is greater than that observed for the K-band of benzaldehyde and, indeed, of any other mono-substituted benzene derivative. (For additional spectroscopic evidence, see below.)

(b) *Phenylacetylene, phenylcyanide*

Both the K-bands of phenylacetylene and of phenylcyanide show fine structure which complicates slightly a comparison with the K-bands of derivatives, in which fine structure is absent or less pronounced. The centre of the band systems (2398 and 2245 Å respectively, in hexane) has been chosen for this purpose. Again, there is no relationship between the polarity or electron-attracting power of the $C{\equiv}CH$ and $C{\equiv}N$ groups and the displacement of the K-band of benzene, the electron polarisability of the more polar $C{\equiv}N$ group being considerably smaller than that of the $C{\equiv}CH$ group. Moreover, the displacements are also smaller (D, 378 and 225 Å respectively, in hexane) than those caused by the $CH{=}CH_2$ and $CH{=}NMe$ groups (430 and 398 Å respectively). The former groups are more strongly electron-attracting, but possess lower electron polarisabilities.

Replacement of hexane by ethanol as solvent has only a negligible effect (~5 Å) on the position of the K-band system of both phenylacetylene and phenylcyanide, in spite of the appreciable polarity of these molecules. This surprisingly small effect indicates either that the electron-shifts in the ground state of the triple bonds, i.e. their *bond* polarisabilities involving changes of the interatomic distances, or only the electron polarisabilities arising from these electron-shifts are negligible (for discussion, see below).

[8] A. Burawoy, *Ber. Dtsch. Chem. Ges.* **64**, 464, 1635 (1931); **65**, 941 (1932); **66**, 228 (1933); *J. Chem. Soc.* 1177 (1939).

TABLE 1. MAXIMA OF K-BANDS IN Å

X	Solvent		$\underrightarrow{C_6H_5—X}$	$\underrightarrow{p\text{-}H_2N—C_6H_4—X}$	$\underleftarrow{p\text{-}O_2N—C_6H_4—X}$
H	EtOH	λ	~2030	2344[5]	2595[5]
		ε	—	8·000	9·500
	C_6H_{14}	λ	~2020[a]	2340	2513
		ε	6·600	7·500	9·000
CH=CH$_2$[b]	EtOH	λ	2453	2770	3010[c]
		ε	15·000	16·000	14·500
		D	+423	+426	+415
		D*	—	+3	—
	C_6H_{14}	λ	2450[a]	2728	2895
		ε	14·000	19·000	15·500
		D	+430	+388	+382
		D*	—	−42	—
CH=NMe	EtOH	λ	2450	2990	2800
		ε	15·000	21·000	17·000
		D	+420	+646	+205
		D*	—	+226	—
	C_6H_{14}	λ	2418	2768	2728
		ε	15·000	23·000	15·000
		D	+398	+428	+215
		D*	—	+30	—
CH=O	EtOH	λ	2445[5]	3315	(2625)[d]
		ε	13·500	26·500	—
		D	+420	+971	(+30)
		D*	—	+551	—
	C_6H_{14}	λ	2408[5,a]	2955	2585[e]
		ε	14·000	22·000	15·000
		D	+388	+615	+72
		D*	—	+227	—
NO=O	EtOH	λ	2595	3725	2601[f]
		ε	9·500	16·800	13·000
		D	+565	+1381	+6
		D*	—	+816	—
	C_6H_{14}	λ	2513[a]	3203	2556
		ε	9·000	14·000	13·500
		D	+493	+863	+43
		D*	—	+370	—
C≡CH	EtOH	λ	2346, 2444 2395[g]	2697	2860
		ε	15·000, 13·500	20·500	15·000
		D	+365	+353	+265
		D*	—	−12	—

Table 1—*continued*

X	Solvent		$\xrightarrow{C_6H_5-X}$	$\xrightarrow{p\text{-}H_2N-C_6H_4-X}$	$\xleftarrow{p\text{-}O_2N-C_6H_4-X}$
	C_6H_{14}	λ	2351, 2446 2398^{a,g}	2650	2798
		ε	15·500, 14·500	20·500	16·000
		D	+378	+310	+285
		D*	—	−68	—
C≡N	EtOH	λ	2217, 2300 2250^{g}	2775	2575^{h}
		ε	13·000, 11·000	24·000	14·000
		D	+220	+431	−20
		D*	—	+211	—
	C_6H_{14}	λ	2210, 2296 2245^{a,g}	2610	2530
		ε	12·000, 11·000	21·000	13·000
		D	+225	+266	+17
		D*	—	+41	—

D* Increase of displacement by the substituent X as compared with the displacement in the mono-substituted benzene derivative.

[a] For data obtained by Klevens and Platt[11] in heptane solution, see Table 2. [b] Data for styrene and its derivatives are also reported by Pestemer *et al.*[9] [c] Kamlet and Glover[10] give 300 mμ in methanol. [d] Spectrum not obtainable owing to acetal formation. Data extrapolated from those obtained for *p*-nitroacetophenone. [e] Pestemer, *et al.*[9] give 258 mμ. [f] Schubert *et al.*[12] give 260 mμ in 95% ethanol. [g] Estimated centre of band system. [h] Schubert *et al.*[12] give 257 mμ in 95% ethanol.

PARA-SUBSTITUTED ANILINE DERIVATIVES

Data for the maxima of the K-bands of aniline and its derivatives substituted in the *para* position by the CH═CH$_2$, CH═NMe, CH═O, NO═O, C≡CH and C≡N groups in hexane and ethanol, the displacements (D) of the maxima on introduction of these substituents, and the differences of the displacements observed in the benzene series and the aniline series (D*) are shown in the second column of Table 1. The effective electron migration is directed, as in the benzene derivatives, towards the substituent as indicated by the long arrow in (IV).

$$\xrightarrow{p\text{-}H_2N-C_6H_4-X} \quad (\mathrm{X{:}\ CH{=}CH_2,\ CH{=}NMe,\ CH{=}O,\ NO{=}O,\ C{\equiv}CH,\ C{\equiv}N}) \quad \mathrm{IV}$$

The displacements (D) of the K-band of aniline (2340 Å in hexane; 2344 Å in ethanol) to longer wavelengths on introduction of the CH═CH$_2$ and C≡CH substituents are slightly smaller, but on introduction of the more polar CH═NMe, CH═O, NO═O and C≡N substituents are considerably greater than those observed in the benzene series. The differences in the displacements (D*) increase with the electron-attracting character of the substituents, i.e. in the order CH═CH$_2$ (−42 Å

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[9] M. Pestemer, T. Langer and F. Manchen, *Monatsh. Chem.* **68**, 326 (1936).

[10] M. J. Kamlet and D. J. Glover, *J. Amer. Chem. Soc.* **77**, 5696 (1955).

[11] H. B. Klevens and J. R. Platt, *Technical Report*, Part I. Office of Naval Research (1953–54); *Chem. Rev.* **41**, 301 (1947); *J. Chem. Phys.* **16**, 832 (1948).

[12] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.* **22**, 1285 (1957).

in hexane; +3 Å in ethanol) < $CH{=}NMe$ (+30; +226 Å) < $CH{=}O$ (+227; +551 Å) < $NO{=}O$ (+370; +816 Å) and $C{\equiv}CH$ (−68; −12 Å) < $C{\equiv}N$ (+41; +211 Å). It will also be observed that this effect is considerably greater in ethanol than in the unpolar hexane as solvent.

The band displacements (D) coincide in the aniline series more closely with the polarity of the absorbing molecules. Thus, in hexane solution, the K-bands are displaced to longer wavelengths in the order *p*-aminostyrene (2728 Å) < *p*-amino-N-methylbenzaldimide (2768 Å) < *p*-aminobenzaldehyde (2955 Å) < *p*-nitroaniline (3203 Å) and the differences are even greater for ethanolic solutions (2770, 2990, 3315 and 3725 Å respectively).

Similarly, whereas the K-band of phenylcyanide (2245 Å in hexane; 2250 Å in ethanol) appears at much shorter wavelengths than that of phenylacetylene (2398 and 2395 Å respectively), *p*-aminophenylcyanide absorbs in hexane at only slightly shorter wavelengths (2610 Å) and in ethanol at considerably longer wavelengths (2775 Å) than *p*-aminophenylacetylene (2650 and 2697 Å respectively). Again, whereas the K-band of styrene (2450 Å in hexane and 2453 Å in ethanol) appears at considerably longer wavelengths than that of phenylcyanide (2245 and 2250 Å respectively), the positions of the K-bands of the corresponding aniline derivatives in ethanol are almost identical (2770 and 2775 Å respectively).

These observations are accounted for by the consideration of two factors:

(i) The terminal electron-repelling amino group and the electron-attracting substituents (IV, X) are responsible for (reinforced) electron-shifts within the aniline derivatives, i.e. the polarities of the terminal groups will be considerably greater than those in aniline and in the benzene derivatives $C_6H_5{-}X$ respectively.* The electron shifts become more pronounced as the electron-attracting power of the substituents (IV, X) increases and as hexane is replaced by the more polar (and possibly hydrogen-bonding) ethanol. They coincide with the direction of the effective charge migration of the transition and, thus, are responsible for increased electron polarisabilities and the resulting displacements of the K-bands to longer wavelengths.

(ii) In absence of any change in the polarity of the substituted absorbing system, the stabilisation of the normal excited state which results from the perturbation (in the excited state) by the electronic system of any substituent, decreases as the length (the number of electrons or possibly the polarisability) of the substituted system increases. This is a generalisation of the well-known fact that the red-shift of a K-band on replacement of a terminal C—H group by the more strongly polarisable $C{-}CH{=}CH_2$ group decreases as the substituted absorbing (conjugated) system is lengthened. For the same reason, this effect is smaller on introduction of a substituent into the *para* position of aniline than into benzene.

This factor will tend to reduce somewhat the discussed bathochromic band displacements to be expected from the increased polarity of the *p*-aniline derivatives and accounts for the negative values of D* observed for the least polar *p*-aminostyrene and *p*-aminophenylacetylene. A more systematic investigation and discussion of this matter will be given in the next communication of this series.

It is noteworthy that the negative value of D* is greater for the K-band of *p*-aminophenylacetylene (−68 Å in hexane; −12 Å in ethanol) than for the K-band of the

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* This is generally attributed to increased contributions of polar structures such as $H_2\overset{+}{N}{=}C_6H_4{=}CH{-}O^-$ but are considered by us to involve inductive electron displacements only.

less polar *p*-aminostyrene (−42; +3 Å) and that the values of D* for *p*-aminophenylcyanide (+41; +211 Å) and *p*-amino-N-methylbenzaldimide (+30; +226 Å) are similar, in spite of the great polarity of the former. Moreover, the bathochromic displacement on replacing hexane by ethanol as solvent is of the same order for the K-bands of the former two substances (47 and 42 Å respectively) and considerably smaller for the K-band of the more polar *p*-aminophenylcyanide (165 Å) than for the K-band of *p*-amino-N-methylbenzaldimide (222 Å). These observations again indicate that in triple bonds the electron-shifts in the ground state are either smaller or at least are responsible for smaller increases of their electron polarisabilities (for discussion, see below).

PARA-SUBSTITUTED NITROBENZENE DERIVATIVES

Data for the maxima and intensities of the K-bands of nitrobenzene and its *para*-substituted derivatives in hexane and ethanol, and the displacements (D) on introduction of the substituents into nitrobenzene are, again, enumerated in Table 1. The effective charge migration in all investigated nitrobenzene derivatives is towards the nitro group, i.e. in contrast to the benzene and aniline derivatives the double and triple bonded substituents are now electron-donating terminal groups [see (V)].

$$\xleftarrow{p\text{-}O_2N-C_6H_4-X} \quad (X\text{: } CH{=}CH_2,\ CH{=}NMe,\ CH{=}O,\ NO{=}O,\ C{\equiv}CH,\ C{\equiv}N) \quad \text{V}$$

The displacements (D) to longer wavelengths on introduction of the substituents (V, X) into nitrobenzene are always smaller than those observed in the benzene series and fall rapidly in the order CH=CH$_2$ (+382 Å in hexane; +415 Å in ethanol) > CH=NMe (+215; +205 Å) > CH=O (+72; +30 Å) > NO=O (+43; +6 Å) and C≡CH (+285; +265 Å) > C≡N (+17; −20 Å). The K-band of *p*-nitrophenylcyanide in ethanol appears even at shorter wavelengths than that of nitrobenzene in this solvent.

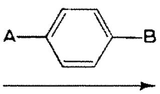
In *p*-nitrostyrene, the nitro group is responsible for an electron-shift in the C—CH=CH$_2$ group which results in an increase of its electron polarisability towards the benzene ring and confers a slightly electron-repelling character to the vinyl group. The greater polarity of *p*-nitrostyrene as compared with nitrobenzene accounts for the slightly larger displacement of the K-band on introduction of the vinyl group in the more polar ethanol (D, +415 Å) than in hexane (D, +382 Å). However, it should be noted that this displacement is in both solvents slightly smaller than that observed for the K-band of styrene (430; 423 Å). As already explained in discussing *p*-aminostyrene, the effect due to the (increased) electron polarisability of the vinyl group in *p*-nitrostyrene is masked by the reduced perturbation effect on substitution of the longer conjugated system of nitrobenzene as compared with that of benzene.

In contrast to the vinyl group, the substituents in all other investigated nitrobenzene derivatives preserve their electron-attracting character. The polarity of these compounds is smaller than that of nitrobenzene itself and, thus, the displacements of the K-bands on introduction of these substituents are smaller in ethanol than in hexane.

The rapid decrease of the band displacements in the order of the electron-attracting power of the substituents is due partly to a decreasing electron polarisability of the substituents towards the *p*-nitrophenyl group and partly to increasing electron-shifts in the substituted O$_2$N—C$_6$H$_4$— system towards the substituent, i.e. in the direction opposite to that of the effective charge migration of the transition. These contributions cannot be easily separated.

ORIGIN OF THE 2000 Å AND 1800 Å BAND SYSTEMS OF BENZENE

The present investigation completes the discussion of the effect of the more important terminal groups of absorbing (conjugated) systems on the corresponding K-bands. Our analysis confirms earlier conclusions[13] that, quite independent of any detailed theoretical interpretation, the band system of benzene at approximately 2000 Å corresponds to the K-bands of the investigated benzene derivatives and, thus originates in the same allowed transition across the benzene system as indicated by the long arrow in (VI) (A=B=H) (for a more precise interpretation, see reference [2]). This excited state of benzene possesses approximately the symmetry $^1E_{1u}$.



VI

The spectrum of benzene shows, in addition to the K-band system at 2000 Å, a band system of much higher intensity at approximately 1800 Å which according to the invaluable determinations of the vacuum ultra-violet spectra by Price and Walsh[14] and by Klevens and Platt[11] reappears, slightly displaced, in all investigated benzene derivatives. The correspondence of these two band systems of benzene with those observed in the spectra of monosubstituted benzene derivatives is convincingly shown by the data and, even more, by the figures recently published by Klevens and Platt. Some of these data are reproduced in Table 2, together with the displacements (D) on introduction of the various substituents.

TABLE 2. MAXIMA IN Å AND INTENSITIES OF THE K-BANDS AND RYDBERG-BANDS OF SUBSTANCES C_6H_5—X

X	K-band			Rydberg-band		
	λ	ε	D	λ	ε	D
H	2020	6·600	—	1834	46·000	—
Cl	2146	7·500	126	1898	54·000	64
Br	2150	8·000	130	1908	36·000	74
I	2278	11·500[6]	258	1946	90·000	112
$CH{=}CH_2$	2463	15·000	443	2033	23·000	199
$CH{=}O$	2404	15·000	384	2004	26·000	170
$C{\equiv}CH$	2386	16·000	366	1992	30·000	158
$C{\equiv}N$	2223	17·000	203	1880	44·000	46
$NO{=}O$	2513	8·000	493	2062	13·000	228
HO	2128	6·000	108	1898	50·000	64
H_2N	2353	8·000	333	1968	32·000	134

The 1800 Å band system of benzene and, thus, the corresponding bands of the benzene derivatives should be assigned to Rydberg transitions originating in the double bonds of benzene.[13] This interpretation is in agreement with the high intensities

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[13] A. Burawoy, *Disc. Faraday Soc.* **9**, 73 (1950).

[14] W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* A **191**, 22, 32 (1947).

of these bands. It also accounts for the much smaller band displacements observed on introduction of substituents, since the symmetry characteristic for a Rydberg transition which is probably localised in only one of the double bonds of benzene (nodal plane in the bond axis) is different from the symmetry of the "unperturbed" states involving the excited electrons of the substituents (nodal plane perpendicular to the bond axis). This should result in a smaller degree of interaction.

Attempts to account for the excited states of benzene by the application of mathematical methods have led to the conclusion that the 2000 Å band system, in spite of its rather high intensity (ε, 6000–7000), corresponds to a forbidden transition ($^1B_{1u}$ or $^1E_{2g}$) and that it is the band system at 1800 Å which may correspond to an excited state of symmetry $^1E_{1u}$ (characteristic for K-bands).

Kauzmann[15] has summarised the conclusions of a very detailed and critical analysis of these methods to which reference should be made: "The theoretical account of the spectrum of benzene is therefore only partially satisfactory. There seems to be little doubt that the lowest excited singlet state is of the $^1B_{2u}$-type, that a triplet state should lie somewhere below it, and that there is a $^1E_{1u}$-level at some distance above it. Other details of the energy level diagram are, however, still not at all clear, and it is doubtful if calculations capable of resolving these uncertainties are feasible at the present time." Obviously, the results of mathematical calculations cannot be taken to represent evidence for the correct assignment of the 2000 Å and 1800 Å band system of the benzene spectrum.

It is, therefore, most significant that the assignments of the band systems arrived at by the mathematical methods are already *qualitatively* in disagreement with the available experimental observations, the empirical comparative analysis of which allows no doubt that the excited state of symmetry type $^1E_{1u}$ corresponds to the 2000 Å band system and not to the 1800 Å band system, and that the latter involves electronic transitions of the Rydberg type.

This lends strong support to the view[1] that, apart from the limitations and inadequacies of the mathematical methods discussed by Kauzmann, the simplifying qualitative structural assumptions such as the consideration of the π-electrons only and their "vertical"* arrangement in non-localised orbitals—which form the common basis of all approximations hitherto applied to the interpretation of more complicated structures such as benzene—are also at fault. These assumptions only *appear* to be justified because electronic repulsions (and related polarisation effects) are insufficiently considered.

GENERAL DISCUSSION

The theoretical interpretation of electronic spectra of organic molecules and, in particular, of the effect of terminal groups of absorbing (conjugated) systems on the position of K-bands advanced in the preceding papers of this series accounts consistently for the observations reported in the present communication.

The wave-mechanical resonance characteristic for the electronic perturbations in the excited states of polyelectronic systems represents a physical phenomenon which is absent in the ground state.[2] Thus, the introduction of a substituent possessing an electron affinity similar to the hydrogen atom, e.g. the vinyl group in styrene, will be

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* The π-electrons are assumed to be moving within orbitals in the common potential field of the nuclear frame-work of benzene including the σ-electrons, similar to the valency electrons in an atom.

[15] W. Kauzmann, *Quantum Chemistry* pp. 375–478. Academic Press, New York (1957).

responsible in the *ground state* for only a *negligible* change in the electron system of the substituted phenyl group, but displaces the K-band *strongly* to longer wavelengths as a result of the increased perturbation by the electron system of the substituent in the *excited state.*

On the other hand, factors (solvents, substituents, proton addition) responsible for electron-shifts in the ground state of an absorbing system which coincide with the direction of the effective charge migration make an additional contribution to the stability of the normal excited state, i.e. they displace the corresponding K-band to longer wavelengths.

There is, however, no simple relationship between the polarity and the electron polarisability of *different* groups or systems. This has already been shown for all terminal groups C—X,[5,6] in which X is an atom with unshared electrons. The electron polarisability increases both in benzene derivatives C_6H_5—X and in the *p*-aniline derivatives H_2N—C_6H_4—X approximately in the same order of groups C—F < C—H < C—OH < C—Cl < C—Br < C—I < C—NH_2 < C—SH. This order is not related to the polarity of the covalent bonds and, what is more important, is approximately the same, whether these groups are at the electron-donating or the electron-receiving end of the charge migration of the transition.* This is accounted for by the fact that these groups are treated as units and that the polarisability of the bonding electrons is completely masked by the contribution of the increasing polarisability of the unshared electrons in the observed order (the effect of which is mainly transmitted through the covalent bond).

Similarly, the electron polarisabilities of the CH=O group and of the C≡N group in benzaldehyde and phenylcyanide are smaller than those of the CH=CH_2 group and of the C≡CH group in styrene and phenylacetylene respectively, although qualitatively the reduced ionisation potential of the carbon atoms and the increased electron affinity of the participating atom in the more polar bonds could have been expected to be responsible for greater electron polarisabilities.

These observations can be accounted for by assuming that the polarisabilities of the unshared electrons attached to double or triple bonded oxygen and nitrogen atoms are smaller than those of the corresponding bonding C—H electrons. The high effective nuclear charge at atoms participating in double and triple bonds is known to be responsible for shorter and stronger bonds with all substituents including the hydrogen atom. The increase of the binding energies of the non-bonding electrons can be expected to be even greater, since their attraction is not hindered by nuclear repulsions (for discussion of this matter and literature, see reference[1]). In agreement with this interpretation, the difference in the electron polarisabilities of the triple bonded C≡CH and C≡N groups (D, 378 and 225 Å, respectively) is much greater than the difference observed for the corresponding double bonded CH=CH_2 and CH=NMe groups (D, 430 and 398 Å, respectively).

The smaller polarisability of the non-bonding electrons or of the bonding C—H electrons in triple bond groups should also partly account for the observation that the total electron polarisability of these groups is smaller than that of double bond groups, but, in this case, an additional factor should be taken into consideration. As recently[2] pointed out, the excited state of a double bond can be described as a resonance

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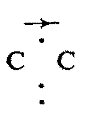
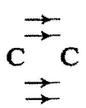
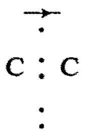
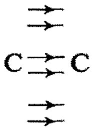
* It should be noted, however, that the electron polarisability of these groups is always considerably greater towards the aromatic carbon atom than in the opposite direction.

hybrid of four equivalent unperturbed excited states each involving one excited electron as indicated in the abbreviating formula (VIII). Its stability will be a function (i) of the stability of each unperturbed excited state (VII) and (ii) of the destabilisation arising from their mutual interactions.


VII


VIII


IX


X

Similarly, the stability of the excited state of a triple bond (X) will be a function of (i) the stability of each unperturbed excited state (IX) and (ii) of the destabilisation arising from the interaction of six such states. Although it is probable that each unperturbed excited state of a triple bond will be more stable (i.e. will involve a smaller transition energy) than that of a double bond, the *destabilisation* should be greater for the triple bond, since it arises from the interaction of the greater number of such states. A mathematical analysis of this matter should be of great interest.

This interpretation also accounts for the observed surprisingly small effect of solvents and polar substituents on the electron polarisability of triple bonds (see above). This cannot be attributed to a negligible transmission of polar effects along triple bonds, since it has been recently[16]* shown that the introduction of an alkyl group into the 3-position of both 1:1-dimethylprop-2-ynyl chloride $HC{\equiv}C{-}CMe_2Cl$ and allyl chloride[17] $H_2C{=}CH{-}CH_2Cl$ has a very appreciable and similar (1000-fold) effect on their rates of ionisation.

However, assuming an equal *total* electron-shift, the shift of each *individual* electron will be smaller in a triple than a double bond. This will result in a smaller increase of the stability of each unperturbed excited state and, thus, of the electron polarisability of the triple bond which effect will be further enhanced by the greater degree of destabilisation arising from the increased interaction of six rather than four unperturbed excited states.

EXPERIMENTAL

The spectral determinations were generally carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high tension spark being employed as the source of light. The spectra of phenylacetylene, phenylcyanide and *p*-aminobenzaldehyde were measured with a Hilger Uvispek Photoelectric Spectrophotometer. All investigated substances were obtained in a high state of purity. *p*-Nitro-N-methylbenzaldimide, *p*-amino-N-methylbenzaldimide and *p*-aminoacetylene have not been previously described.

*p-Nitro-*N*-methylbenzaldimide.* *p*-Nitrobenzaldehyde (15·8 g) and aqueous methylamine (100 cc of a 33% w/v solution) were heated on a water-bath for 30 min. On cooling, the initially formed oil solidified. Yield: 15 g; 85% of theory. *p*-Nitro-N-methylbenzaldimide crystallised from ethanol as small yellow plates of m.p. 106°. (Found: C, 58·8; H, 5·0; N, 17·0; Calc. for $C_8H_8N_2O_2$: C, 58·5; H, 4·9; N, 16·4%).

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[*] The rate of hydrolysis of allyl chloride [given as 10^4k_1 (sec^{-1})] reproduced in Table 1 of this paper should be 0·00036 and not, as printed, 0·000036.

[16] A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954).

[17] C. A. Vernon, *J. Chem. Soc.* 423 (1954).

p-*Amino*-N-*methylbenzaldimide*. A solution of *p*-aminobenzaldehyde (10·0 g) in an excess of aqueous methylamine (33% w/v) was allowed to stand for 20 hr. The solvent was evaporated over potassium hydroxide in vacuo. The residue consisting of almost pure *p*-amino-N-methylbenzaldimide crystallised from aqueous methylamine as colourless needles of m.p. 90–91°. Yield: 9·0 g, 80% of theory. Exposed to air, the crystals soon turned yellow (probably due to salt formation with carbonic acid). (Found: C, 71·4; H, 7·6; Calc. for $C_8H_{10}N_2$: C, 71·6; N, 7·4%).

p-*Aminophenylacetylene*. *p*-Nitrophenylacetylene[18] (10 g) was shaken for 24 hr with zinc dust (3·0 g), ammonia (4 cc, 0·88 sp. g.), and water (3 cc) at room temp., water-cooling being applied at the onset of the reaction. The mixture was steam-distilled and the distillate extracted with ether. After removal of ether, the residue of almost pure *p*-aminophenylacetylene was collected. Yield: 0·72 g, 90% of theory. Crystallisation from light petroleum (b.p. 60–80°) gave colourless needles of m.p. 100°. (Found: C, 82·4; H, 5·8; N, 12·0; Calc. for C_8H_7N: C, 82·1; H, 5·9; N, 12·0%).

Acknowledgements—We wish to thank Mr. B. Manohin for the microanalyses carried out in connection with this investigation and the Department of Scientific and Industrial Research for a maintenance grant to one of us (J. P. C.).

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[18] V. B. Drewson, *Liebigs Ann.* **211**, 150 (1882).