832. *Electronic Spectra of Organic Molecules and their Interpretation. Part II.* Effect of Terminal Halogen Atoms of Conjugated Systems on* K-*Bands.*†

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The effect of halogen atoms at the ends of the conjugated systems (1) and (2) on the position of the corresponding *K*-bands is studied,

$$(1)\ \underrightarrow{p\text{-Hal}\cdot C_6H_4\cdot B}\ (B = H, \overset{+}{N}H_3, CHO, CH{:}\overset{+}{O}H, NO_2)$$

$$(2)\ \underrightarrow{p\text{-A}\cdot C_6H_4\cdot \text{Hal}}\ (A = Ph, OMe, O^-, NH_2, I)$$

The *K*-bands are displaced to longer wavelengths with increasing polarisability of the C–Hal electrons, *i.e.*, in the order C–F ⟶ C–I (in both directions) and to a smaller degree with increasing polarity (and resulting polarisability) of the absorbing system in the direction of the " effective " electronic migration of the transition. The polarisability of the C–F electrons towards the fluorine atom is appreciably smaller than that of the C–H electrons towards hydrogen, resulting in a blue-shift of the *K*-bands in system (2). A comparison of the *K*-bands of the *p*-halogenobenzaldehydes and their conjugate acids indicates that with increasing electron demand by the carbon atom the electron shift in the ground state increases in the order C–F ⟶ C–I. The reported observations cannot be explained with the help of structures involving non-localised bonds, and mesomeric (electromeric) electron displacements, and by consideration of π electrons only, but are consistently accounted for by inductomeric electron displacements in systems built up of localised bonds only.

AN investigation of the effect of terminal methyl and substituted methyl groups (A or B) of conjugated systems (I) on the position of the corresponding *K*-bands [1] has reaffirmed that the observations related to the electronic spectra of organic compounds cannot be accounted for by the widely accepted theoretical interpretations based on molecular structures involving non-localised bonds (many-centred orbitals) and on the simplifying assumption that only the π electrons are important or need to be considered for the electronic transitions. However, they can be understood with the help of classical structures involving only localised bonds and inductive electron displacements.[2, 3]

On this basis, an absorbing (conjugated) system (such as I) can be considered as a system of interacting smaller polarisable units (electron pairs or even the single electrons). The electron migration along the absorbing system which corresponds to the transition responsible for a *K*-band is facilitated by an increase in the polarity of the individual bonds

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* Part I, *J.*, 1955, 2557.

† Submitted in honour of the seventieth birthday of Sir Ian Heilbron, D.S.O., F.R.S.

[1] Burawoy and Spinner, *J.*, 1955, 2557.

[2] Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537; *Discuss. Faraday Soc.*, 1951, **10**, 104; *Chem. and Ind.*, 1944, 434; " Contribution to the Study of Molecular Structure," Desoer, Liège, 1947—1948, p. 73.

[3] Burawoy and Spinner, *J.*, 1954, 5438.

or by their replacement by other more strongly polarisable units. This will stabilise the excited state and cause a red-shift of the *K*-band. Thus, the effect of any terminal atom or group (I; A or B) will be due mainly to two factors, the degree of the polarisability of its electron system and the change of the polarity of the substituted system.

(I) $A{\cdot}[CH{=}CH]_n{\cdot}B$

Experimental evidence has also been given [1] that the " effective " electron migration in one direction along the absorbing system determines the stability of the excited state, *i.e.*, that in qualitative comparative discussions of electronic spectra the accompanying (complementary) electron migration in the opposite direction can generally be neglected (cf., however, below). In the present paper, the discussion is extended to the effect of terminal halogen atoms (I; A or B = F, Cl, Br, I) on the position of the corresponding *K*-bands.

The polarity of the C–Hal bonds in alkyl halides is known to increase in the order $C{-}I \ll C{-}Br < C{-}Cl \ll C{-}F$. It is reduced in the halogenoethylenes, halogenobenzenes, and other systems, in which the halogen atom is attached to a carbon atom participating in a multiple linkage. As already shown,[2,3] this involves inductive electron displacements (accompanied by changes of the interatomic distances) resulting from the increased effective nuclear charge (electron deficiency) at such carbon atoms, rather than a delocalisation of the unshared electrons of the halogen atoms (mesomeric effect). The greater acidity of the halogenobenzoic acids and halogenophenylacetic acids than of the parent acids [4] shows that the halogen atoms in these compounds are still electron attracting. There is no reason to suppose that in other comparable series the polarity of the C–Hal bonds is reversed or that, as the electron demand by the carbon atom increases, the normal order of the C–Hal polarities becomes inverted, *i.e.*, that the reduction of the polarity increases in the order $C{-}I < C{-}Br < C{-}Cl < C{-}F$.

Observations such as the smaller acidity of *p*-fluorophenol ($10^{10}K$, 0·26) than of phenol (0·32) or the increasing acidity of the *p*-halogenophenols in the order F (0·26) < Cl (1·32) < Br (1·55) < I (2·19) [4] do not represent such evidence. Equilibria or rates of chemical reactions are determined not only by the polar effects of the halogen atoms (or other substituents), but also, often decisively, by the differences of the C–Hal bond energies in the two entities involved, *i.e.*, the stabilisation energies and bond contractions resulting from an increased electron demand.[2,3] These observations show conclusively only that the stabilisation energies increase in the order $C{-}I < C{-}Br < C{-}Cl < C{-}F$, but do not give information about the accompanying relative changes of the bond polarities. It has been one aim of the present investigation to elucidate this matter.

We have determined the electronic spectra in ethanol and in hexane of the halogenobenzenes, of diphenyl, anisole, aniline, iodobenzene, nitrobenzene, benzaldehyde and their *p*-halogeno-derivatives, in 99% ethanol of the *p*-halogenoanilinium ions, and in ethanol and water of the *p*-halogenophenoxide ions, and the spectra of the conjugate acids of the benzaldehydes in concentrated sulphuric acid. Data for the positions and molecular extinction coefficients of the maxima of the *K*-bands as well as the displacements in Å units caused by the halogen atoms are shown in Table 1. Our determinations were carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, but most data have also been confirmed with a Hilger Uvispek photoelectric spectrophotometer. The reported data below 2190 Å have been obtained by the latter method. The experimental error is not more than 5 Å in the position of the maxima and 10% in the molecular extinction coefficient. The order of the differences (sometimes only small) between the parent substances and the fluoro-derivatives on the one hand and of the chloro- and bromo-derivatives on the other is certain. The position of the *K*-band of benzene has been taken to be 2030 Å in ethanol and 2020 Å in hexane, 2035 Å in water and 2020 Å in heptane being reported by Doub and Vandenbelt [5] and by Platt and Klevens,[6] respectively.

Halogenobenzenes.—The *K*-band of benzene is displaced to longer wavelengths in the

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[4] Dippy, *Chem. Reviews*, 1939, **35**, 151.
[5] Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.
[6] Klevens and Platt, Tech. Rept. 1953—1954, Part I, Office of Naval Research.

TABLE 1. *Maxima (in* Å) *of* K-*bands of* p-R·C_6H_4·X.

R	Solv.	X =	H	F	Cl	Br	I
H	EtOH [a]	λ	~2030	2068	2130 *	2135 *	2275 [b]
		ε	—	3000	6100	7300	12,000
		D	—	+38	+100	+105	+245
	C_6H_{14} [c]	λ	~2020	2068	2152	2160	2300 *[d]
		ε	6600	3000	7600	7700	11,500
		D	—	+48	+132	+140	+280
NH_3^+	EtOH–HCl (99 : 1)	λ	—	2078	2167	2190	2324
		ε	—	3400	8000	8400	12,500
Ph	EtOH	λ	2475	2462	2550	2562	2586
		ε	19,500	18,600	23,500	25,500	25,500
		D	—	−13	+75	+87	+111
	C_6H_{14}	λ	2467	2450	2527	2540	2573
		ε	19,000	16,000	20,500	22,000	22,000
		D	—	−17	+60	+73	+106
I	EtOH	λ	2275	2258	2359	2374	2416
		ε	12,000	10,500	17,000	17,500	18,500
		D	—	−17	+84	+99	+141
	C_6H_{14}	λ	2300 *	2262	2363	2390 *	2425
		ε	11,000	10,500	16,000	16,500	17,500
		D	—	−38	+63	+90	+125
NH_2 [e]	EtOH	λ	2344	2334	2445	2452	2502
		ε	8000	7000	12,500	13,500	18,500
		D	—	−10	+101	+108	+158
	C_6H_{14}	λ	2340	2305	2414	2418	2463
		ε	7500	7000	12,500	13,000	17,500
		D	—	−35	+73	+78	+123
MeO	EtOH	λ	2195 [f]	2170	2282	2274	2335
		ε	7500	6800	11,500	12,000	16,000
		D	—	−25	+87	+79	+140
	C_6H_{14}	λ	2198 [f]	2163	2280	2270	2339
		ε	7000	5700	11,000	11,500	15,500
		D	—	−35	+82	+72	+141
O^-	0·1% NaOEt in EtOH	λ	2374	2350	2465	2454	2500
		ε	12,500	7500	12,500	17,000	19,000
		D	—	−24	+91	+80	+126
	0·1N-NaOH	λ	2345	2318	2446	2440	2473
		ε	11,000	6000	11,000	11,500	16,000
		D	—	−27	+101	+95	+128
NO_2	EtOH	λ	2595	2622	2699	2755	2940
		ε	9500	9000	11,000	11,500	12,500
		D	—	+27	+104	+160	+345
	C_6H_{14} [g]	λ	2513	2569	2652	2697	2865
		ε	9000	8200	11,000	11,500	12,500
		D	—	+56	+139	+184	+352
CHO	EtOH	λ	2445	2461	2544	2591	2708
		ε	13,000	11,500	16,000	16,500	13,500
		D	—	+16	+99	+146	+263
	C_6H_{14}	λ	2408	2439	2529	2575	2695
		ε	14,000	13,000	17,500	18,500	15,500
		D	—	+31	+121	+167	+287
CH:OH$^+$	H_2SO_4	λ	2950	2990	3195	3327	3718
		ε	26,000	23,000	30,000	27,500	21,500
		D	—	+40	+245	+377	+768

* Centre of broad band indicating fine structure.

[a] Bowden and Braude (*J.*, 1952, 1068) give 2040, 2100, 2100, and 2260 Å, respectively, for the halogenobenzenes. [b] Ungnade (ref. 7) gives 227 mμ in *cyclo*hexane. [c] Klevens and Platt (ref. 6) give 2146, 2150, and 2278 Å (1st band) for heptane solutions of chloro-, bromo-, and iodo-benzene, respectively. [d] Ungnade (*loc. cit.*) gives 2286 and 2335 Å in *cyclo*hexane. [e] Doub and Vandenbelt (ref. 5) give 230, 239, and 239·5 mμ for aqueous solutions of aniline and *p*-chloro- and *p*-bromo-aniline, respectively. [f] Ungnade (*loc. cit.*) gives 220 and 222 mμ in ethanol and *cyclo*hexane, respectively. [g] Conrad-Billroth, Förster, and Wagner (*Z. phys. Chem.*, 1937, *B*, **35**, 343) give 2560, 2646, and 2680 Å for *p*-fluoro-, *p*-chloro-, and *p*-bromo-nitrobenzene, respectively. Ungnade (*J. Amer. Chem. Soc.*, 1954, **76**, 160) gives spectra of the *p*-halogenonitrobenzenes in 95% ethanol, and Ferguson and Iredale (*J.*, 1953, 2959) those of *p*-fluoro-, -chloro-, and -bromo-iodobenzene in light petroleum.

order of substituents, F (*D*, 48 and 38 Å, in hexane and ethanol, respectively) < Cl (*D*, 132 and 100 Å) < Br (*D*, 140 and 105 Å) < I (*D*, 280 and 245 Å). The direction of the effective electron migration of the transition in the halogenobenzenes is towards the phenyl group (II). This follows unambiguously (i) from the displacement of their *K*-bands in ethanol to longer wavelengths (10, 37, 55, 49 Å) in the corresponding *p*-halogenoanilinium ions (see Table 1), the effective electron migration being facilitated by the electron shift (in the ground state) in its direction on introduction of the electron-attracting ammonium group, and (ii) from the displacement of the *K*-bands to shorter wavelengths on replacing hexane by ethanol which is responsible for an electron shift in the opposite direction.

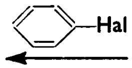
The electron shift in the phenyl group due to the electron-attracting terminal halogen atoms reduces its polarisability, but this effect is masked by the considerably greater polarisability of the C–Hal electrons towards the carbon atom (increasing in the order C–F < C–Cl < C–Br < C–I). The greater electron polarisability [1] of the aliphatic C–Hal system towards the halogen atom than in the opposite direction is reversed as a result of the reduction of the polarity in the aromatic C–Hal bonds (including the shift of the unshared electrons). Whilst the electronic polarisability, being mainly a function of the ionisation potentials and electron affinities of the atoms of a bond, should, in principle, be expected to be greater towards the negative end of the dipole, in the aromatic C–Hal systems (which are treated as a unit) this effect is masked by the contribution of the greater polarisability of the unshared electrons in the opposite direction.

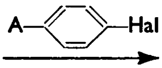
TABLE 2. *Differences* (*in* Å) *in the position of* K-*bands of* p-R·C_6H_4·X *in hexane and ethanol.* (*D*, Observed displacement. *D′*, Displacement attributed to C–Hal system.)

X =	H	F		Cl		Br		I	
R	*D*	*D*	*D′*	*D*	*D′*	*D*	*D′*	*D*	*D′*
(i) H	+10	0	−10	−22	−32	−25	−35	−25	−35
(ii) Ph	+8	+12	+4	+23	+15	+22	+14	+13	+5
(iii) I	−25	−4	+21	−4	+21	−16	+ 9	− 9	+16
(iv) NH_2	+4	+29	+25	+31	+27	+34	+30	+39	+35
(v) MeO	−3	+7	+10	+2	+5	+4	+7	−4	−1
(vi) NO_2	+82	+53	−29	+47	−35	+58	−24	+75	−7
(vii) CHO	+37	+22	−15	+15	−22	+16	−21	+13	−24

p-*Halogeno-derivatives of Diphenyl, Iodobenzene, Aniline, Anisole, and the Phenoxide Ion.*—The effective electron migration of the *K*-band transition in these compounds is determined by the terminal phenyl, iodo, amino, methoxyl, and charged oxygen substituents, respectively, and is directed towards the halogen atom (III).

(II)





(A = Ph, NH_2, I, OMe, O^-) (III)

Thus, in contrast to the halogenobenzenes, on replacing hexane by ethanol the electron shift in the ground state facilitates the effective electron migration of the C–Hal electrons resulting in bathochromic displacements of the *K*-bands. Data for these displacements (*D′*) representing the difference between the displacements (*D*) observed for the parent substances and the corresponding halogen derivatives, are shown in Table 2, (ii)—(v). They are mainly due to a change of the polarity of the absorbing molecules in the ground state, but there is no evidence to show whether, in addition to the dielectric properties of the solvent, any stoicheiometric hydrogen-bond formation of the halogen atoms with ethanol makes some contribution, as recently suggested by Ungnade.[7]

The direction of the effective electron migration (as in III) is also supported by an analysis of the effect of the methoxyl, amino, iodo, and charged oxygen substituents in the *para*-position on the *K*-bands of the halogenobenzenes (cf. Table 3). The red-shifts are considerably greater than those to be expected for these substituents on the " receiving " end of the effective electron migration. As will be more fully discussed in a subsequent publication, the corresponding displacements are, *e.g.*, for the methoxyl group in *p*-anisidine

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[7] Ungnade, *J. Amer. Chem. Soc.*, 1953, **75**, 432.

10 and 30 Å, for the amino-group in *p*-phenylenediamine 96 and 119 Å, for the iodine atom in *p*-iodoaniline 158 and 123 Å, and for the negatively charged oxygen atom in the dibasic salt of quinol, 65 Å (in water) (cf. Table 3). (They should be even smaller, if the change of polarity due to the electron-attracting halogen atoms is taken into account.)

TABLE 3. *Displacements* (Å) *of the maxima of* K-*bands of* p-R·C_6H_4·X *by* R.

R =	OMe		NH_2		O^-	I	
X	EtOH	C_6H_{14}	EtOH	C_6H_{14}	EtOH	EtOH	C_6H_{14}
F	102	95	266	237	282	190	194
Cl	152	128	315	262	335	229	211
Br	139	110	317	258	319	239	230
I	60	39	227	163	225	141	125
NH_2	10	30	96	119	65 *	158	123

* O^-·C_6H_4·O^- in 1N-sodium hydroxide (and sodium hydrogen sulphite).

The *K*-bands of these halogeno-derivatives are displaced in all series to longer wavelengths in the order $F < Cl \lesssim Br < I$ showing that the contribution of the increasing polarisability of the C–Hal electrons is more important than that of the change in the polarity of the substituted system which would require increasing displacements in the reverse order. However, in these series the red-shifts due to the chloro-, bromo-, and iodo-substituents (60—101, 72—108, and 106—158 Å, respectively) are smaller than those observed in the halogenobenzenes, even although the effect due to the C–Hal polarisability is now reinforced by that due to the increased polarity of the substituted system. This confirms that the polarisability of the aromatic C–Hal electrons is appreciably greater in direction towards the carbon atom.

The contribution of the polarity factor is indicated by the slightly greater red-shift of the *K*-band of anisole and the phenoxide ion on introduction of the more strongly electron-attracting chlorine than of bromine, which order has not been observed previously. It should also be responsible for the remarkable observation that the effective electron migration in the halogenodiphenyls is in the opposite direction to that in the halogenobenzenes. This is established not only by the much smaller bathochromic displacements of the *K*-bands on introduction of the chlorine, bromine, and iodine atoms and the blue-shift on introduction of the fluorine atom (cf. below) into diphenyl, but also by the opposing effect of solvents in these two series. The electron-shift in the ground state in the C_6H_5·C group on introduction of the electron-attracting halogen atoms increases its polarisability towards the halogen atom and reduces it in the opposite direction, this contribution resulting in a reversal of the relative polarisabilities of the whole absorbing system. This matter is being further investigated.

As will be shown elsewhere, the only small difference in the position of the *K*-bands of chlorobenzene and bromobenzene (5—8 Å) and the fact that the *p*-bromo-derivatives of aniline, diphenyl, and iodobenzene absorb at slightly longer wavelengths than the corresponding chloro-derivatives (5—15 Å) can be attributed to a small contribution of the complementary electron migration of the transition which in the comparison of very small differences cannot be completely neglected.

Effect of the Fluorine Atom.—The *K*-band of fluorobenzene in ethanol and hexane appears at 2068 Å, *i.e.*, at longer wavelengths than that of benzene. This is in agreement with observations by Hammond, Price, Teegan, and Walsh,[8] and by Klevens and Zimring [9] for the gaseous state and the heptane solution, respectively, of this compound.

In contrast, the *p*-fluoro-derivatives of diphenyl, anisole, aniline, and iodobenzene in both hexane and ethanol and those of the phenoxide ion in ethanol and water definitely absorb at shorter wavelengths (by 10—38 Å) than the corresponding parent substances. The increase of polarity of the absorbing systems of these compounds in the direction of the effective electron migration of the *K*-band transition should in itself be responsible for a moderate red-shift of the *K*-band. Thus, the blue shifts observed show that the

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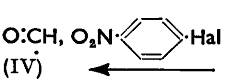
[8] Hammond, Price, Teegan, and Walsh, *Discuss. Faraday Soc.*, 1950, **9**, 53.
[9] Klevens and Zimring, *J. Chim. physique*, 1952, **49**, 377.

polarisability of the C–F electrons in this direction must be appreciably smaller than that of the C–H electrons, the latter group being only arbitrarily chosen as standard owing to its small polarisability and common occurrence in organic compounds.

p-*Halogeno-nitrobenzenes and -benzaldehydes.*—The effective electron migration of the *K*-band transition in nitrobenzene, benzaldehyde, and their *p*-halogen derivatives is towards the nitro or carbonyl group, respectively (as in IV). Thus, the *K*-bands appear at appreciably longer wavelengths in ethanol than in hexane, the displacements being smaller in the less polar halogeno-derivatives [for data of the observed displacements (*D*) and those attributable to the C–Hal bonds (*D*′), see Table 2, (vi) and (vii)].



(IV)

Introduction of the halogen atoms into the *p*-position of nitrobenzene and benzaldehyde is responsible for red-shifts increasing in the order F < Cl < Br < I (*D* in ethanol, 27, 104, 160, 345 Å, and 16, 99, 146, 263 Å, respectively). As in the halogenobenzenes, the small blue-shift to be expected from the reduction of the polarity of the substituted system in the ground state is completely masked by the much more important contribution of the polarisability of the C–Hal electrons. In the nitrobenzene derivatives, the displacements to longer wavelengths are greater than in the benzaldehydes, since in the ground state the more strongly electron-attracting nitro-group is responsible for a greater shift of the C–Hal electrons towards the phenyl group, resulting in their enhanced polarisability in this direction.

A comparison of the red-shifts of the *K*-bands in the spectra of the *p*-halogenobenzaldehydes in ethanol (F, 16; Cl, 99; Br, 146; I, 263 Å) with those observed in the spectra of their conjugate acids in concentrated sulphuric acid (F, 40; Cl, 245; Br, 377; I, 768 Å) is significant. The displacements are not only much greater in the latter, but the increases are appreciably enhanced in this order. The magnitude of this effect allows no doubt that the greater electron demand in the conjugate acids is responsible for an electron shift (in the ground state) increasing in the same order C–F < C–Cl < C–Br < C–I, in which the stabilisation energies (" resonance energies ") are known to decrease. This is similar to the observation [10] that on electron demand the stabilisation energies (which are responsible for the Baker–Nathan effect) decrease, but the polarity changes normally increase in the order C–Me < C–Et < C–Pr^i < C–Bu^t. Our observations show, again, that the relation between bond-energy increases and polarity changes, which is inherent in the interpretation of these effects by the conceptions of mesomerism, hyperconjugation, and other views based on structures involving non-localised bonds, is not even qualitatively valid.

The difficulty, if not impossibility, of explaining electronic spectra with the help of these conceptions is illustrated by the fact that the terminal halogen atoms displace the *K*-bands to longer wavelengths in the order F < Cl $\lesseqgtr$ Br < I, both on the donating and the receiving end of the effective electron migration. In the former case, *i.e.*, in the *p*-halogeno-derivatives of benzene, nitrobenzene, and benzaldehyde, the interpretation of these red-shifts by means of mesomeric or electromeric electron displacements would require and has led to the conclusion that delocalisation increases both in the ground state and the excited state in the order C–F $\longrightarrow$ C–I.[11] However, the stabilisation energies (" resonance energies ") derived from chemical reactions and equilibria show unambiguously (at least in the ground state) that the mesomeric and electromeric effects, if real, increase in the opposite order. These observations illustrate also the general experience that there is no simple relation between the effect of substituents on the stability of the ground state and the excited states of a molecule respectively.

What is even more important, the participation of the terminal halogen atoms at the receiving end of the effective electron migration of the transition as in the *p*-halogen derivatives of anisole, aniline, diphenyl, iodobenzene, and the phenoxide ion cannot be accounted for, since in these excited states (" resonance " structures indicating) delocalisation cannot even be postulated. This is also true for the blue-shifts on introduction of a fluorine atom. The latter cannot be explained by any polar effects, and

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[10] Burawoy and Spinner, *J.*, 1955, 2085.

[11] Murrell and Longuet-Higgins, *Proc. Phys. Soc.*, 1955, *A*, **68**, 329; in this connection see also Price and Walsh, *Proc. Roy. Soc.*, 1947, *A*, **191**, 30, and ref. 8, p. 57.

represent conclusive evidence that even the C–H electrons participate in the electron migration of a transition, their polarisability being greater than that of the C–F electrons in this direction.

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