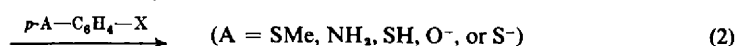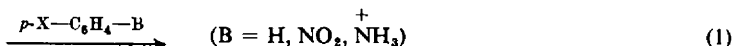# ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—IV*

## EFFECT OF TERMINAL ATOMS WITH LONE ELECTRON PAIRS ON THE K-BANDS OF CONJUGATED SYSTEMS

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**Abstract**—The effect of the hydroxyl, methoxyl, mercapto, methylmercapto, and amino groups as well as of the charged $O^-$ and $S^-$ atoms (X) at the ends of the conjugated systems (1) and (2) on the position of the corresponding K-bands is discussed.

$$\xrightarrow{p\text{-}X\text{—}C_6H_4\text{—}B} \qquad (B = H, NO_2, \overset{+}{N}H_3) \qquad (1)$$

$$\xrightarrow{p\text{-}A\text{—}C_6H_4\text{—}X} \qquad (A = SMe, NH_2, SH, O^-, \text{ or } S^-) \qquad (2)$$

The conclusions of earlier investigations are confirmed. The "effective" electron migration in one direction along the absorbing conjugated system (indicated by the long arrow) determines almost exclusively the stability of the observed excited state. The displacement of a K-band to longer wavelengths on introduction of a terminal group (X) can be due either to an electron shift in the substituted system coinciding with the direction of the effective electron migration of the transition or to an increased electron polarisability of the terminal group itself.

A consistent qualitative, but very detailed, theoretical interpretation of these observations is possible by a consideration of the electronic perturbations in the excited state due to Heisenberg resonance, if the molecules are accepted as being built up of localised bonds and involving inductive (inductomeric) electron shifts only.

## 1. INTRODUCTION

Investigations of the effect of terminal methyl groups,[1] substituted methyl groups,[2] and of the halogen atoms[3] of absorbing (conjugated) systems such as (I) on the position of the corresponding absorption bands of high intensity (K-bands) have provided evidence that the "effective" electron migration in one direction along the absorbing system determines the transition energy (stability of the excited state). The contribution of the accompanying "complementary" electron migration in the opposite direction is only small and can, generally, be neglected in qualitative comparative discussions.

$$\xrightarrow{A\text{—}[CH{=}CH]_n\text{—}B} \qquad (A \text{ or } B: CH_3, CH_2X, F, Cl, Br, I)$$
$$I$$
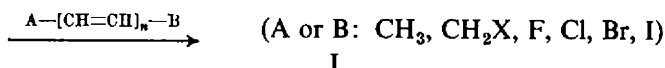
It has also been shown that the displacement of a K-band to longer wavelengths on structural modification of the terminal groups (I, A–C or C–B) can be due to two factors: (a) Electron shifts (in the ground state) of the substituted system which will

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* *Tetrahedron* 2, 122 (1958) is considered as Part III of this series.
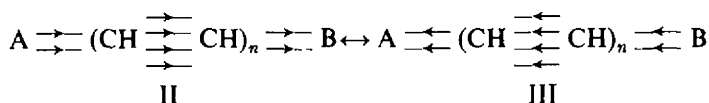[1] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2085 (1955).
[2] A. Burawoy and E. Spinner, *J. Chem. Soc.* 2557 (1955).
[3] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).

increase its electronic polarisability (and facilitate the electron migration) in this direction. (b) An increase of the electronic polarisability of the terminal group itself.

The reported observations cannot be consistently accounted for by the widely-accepted theoretical interpretations based on molecular structures involving non-localised bonds (resonance among several idealised valence-bond structures, many-centred molecular orbitals), on mesomeric electron displacements, and on the simplifying assumption that only the $\pi$ electrons are important or need to be considered for the electronic transition. However, a qualitative, but very detailed, understanding of these and other observations related to the electronic spectra of organic molecules becomes possible by consideration of the mathematically well-established effects resulting from the electronic perturbations in an excited state attributable to Heisenberg resonance, if organic molecules are accepted as being built up of localised bonds and as involving inductive electron shifts only.[4]

According to this view, the normal excited state of a molecule of type (I) corresponding to a K-band can be represented as a "hybrid" of unperturbed states each involving one excited electron. It is possible, for convenience, to indicate this by one formula only (II), in which the excited electron of each unperturbed state is shown by one arrow, simultaneously indicating the symmetry of the excited orbital as well as the direction of the charge migration on one side of the nodal plane formed. Ignoring the branching C—H bonds, the contribution of the $(2 \div 6n)$ unperturbed states to the "hybrid" will be proportional to their stability but, in the first instance, only states involving neighbouring excited electrons will interact.

$$A \rightleftharpoons (CH \rightleftharpoons CH)_n \rightleftharpoons B \leftrightarrow A \rightleftharpoons (CH \rightleftharpoons CH)_n \rightleftharpoons B$$

$$\text{II} \qquad\qquad\qquad\qquad\qquad \text{III}$$

The excited orbital of each unperturbed state is divided by a nodal plane into two parts corresponding to wave-functions of opposite sign. In an unsymmetrical bond, it will extend to a different degree on both sides of the nodal plane formed. In valence-bond terminology, this would be equivalent to the statement that in the excited state of a molecule $\overset{\delta+}{A}$—$\overset{\delta-}{B}$ described as a hybrid $\overset{+}{A}\overset{-}{B} \leftrightarrow \overset{-}{A}\overset{+}{B}$, the stability (and contribution to the hybrid) of $\overset{+}{A}\overset{-}{B}$ is different from and greater than that of $\overset{-}{A}\overset{+}{B}$.

The *degree of interaction* will increase, the lower and energetically nearer each pair of interacting (unperturbed) energy levels are, but, in the first instance, only their part-orbitals in phase with the effective electron migration of the transition, the direction of which is indicated by the arrows, will be important. Thus, if A and B in (II) are identical, e.g. halogen or hydrogen atoms, the unperturbed energy levels involving the excited electrons of the unsymmetrical bonds A—C and C—B will be equal. However, the degree of interaction (determining the degree of stabilisation of the normal excited state) will be different, since it depends on the different extension (stability) of the excited orbital on both sides of the dividing nodal plane. (This corresponds to the different electron polarisability in the two directions of these bonds.)

The factors determining the *stability* of the normal excited state are (i) the most

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

stable (the "basic") unperturbed excited state and (ii) the degree of its interaction with the unperturbed states involving excited neighbouring electrons. Again, the stability of the latter will be modified by interaction with other neighbouring states, the effect of which is transmitted along the whole absorbing system.

The empirical conclusion that the electron migration in one direction of the absorbing system determines the stability of the normal excited state indicates that the additional stabilisation arising from the interactions of the part-orbitals corresponding to the complementary electron migration of the system (cf. III) is only negligible. It should be expected to be greatest if the difference between the two energy levels corresponding to the artificially separated combined part-orbitals of the absorbing system (e.g. II and III) is very small. In such a case, it sometimes becomes apparent and has to be taken into account even in qualitative comparative discussions, if only small differences ($<50$ Å) are under consideration. A more detailed discussion of this matter and experimental evidence for the reality of this effect will be given elsewhere.

This interpretation also accounts for the fact that any electron shift in the ground state of an absorbing system or individual bond (as, e.g., caused by a change of the terminal group or by a solvent) increases the electronic polarisability in the direction of the shift (and reduces it in the opposite direction) and, thus, dependent upon the direction of the effective electron migration of the transition, stabilises (or otherwise) the normal excited state. This indicates that in each bond the increased stability of the part-orbitals in phase with the effective electron migration of the transition, which results from the reduction of the ionisation potential of the "donating" atom and/or the increase in the electron affinity of the "receiving" atom, is the determining factor (for details, cf. reference 4).

In the present paper, the discussion is extended to the effect of terminal groups involving atoms with unshared electrons (other-than the already discussed halogen atoms[3]) (I, A or B = OH, OMe, SH, SMe, NH$_2$, O$^-$, S$^-$) on the position of the corresponding K-bands. However, for purposes of comparison, reference to the effect of the fluorine atom will also be made.

## 2. EFFECT OF ELECTRON-DONATING TERMINAL GROUPS OF THE EFFECTIVE ELECTRON MIGRATION

### (a) *Mono-substituted benzene derivatives*

Data for the maxima and intensities of the K-bands of benzene, fluorobenzene, phenol, anisole, thiophenol, thioanisole, and aniline in hexane and ethanol and of the phenoxide and thiophenoxide ions in ethanol and water, as well as the displacements (D) of the benzene K-band (2020/2035 Å in various solvents) to longer wavelengths on substitution, are shown in Table 1.

The electron-repelling power of the substituents (X) in these compounds (IV) increases approximately in the order F $\ll$ OH $<$ OMe $\sim$ SH $<$ SMe $<$ H $<$ NH$_2$ $\ll$ O$^-$, S$^-$. In phenol, anisole, thiophenol, and thioanisole, the hydroxyl, methoxyl, mercapto, and methylmercapto groups respectively should be slightly electron-attracting compared with the hydrogen atom, since the groups, on introduction into the *m*-position, are known to increase the acidity of phenol and even of benzoic acid.[5]

[5] H. C. Brown, D. H. McDaniel and O. Häfliger, *Determination of Organic Structures by Physical Methods* p. 588. Academic Press, New York (1955).

$$\xleftarrow{\text{C}_6\text{H}_5-\text{X}}$$
$$\text{IV}$$
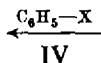
The effective electron migration of the K-band transition is, undoubtedly, in all these examples directed towards the benzene nucleus (indicated by the arrow in IV), since this has already been shown to be true for fluorobenzene.[3] Thus, the electron-shift in the ground state of the substituted phenyl group should make a small decreasing negative contribution in the order $F > OH > OMe \sim SH > SMe > H$ and an increasing positive contribution in the order $H < NH_2 < O^- \sim S^-$ to the observed bathochromic displacement of the benzene K-band, although this effect should be insignificant in the case of the hydroxyl, methoxyl, mercapto, and methylmercapto groups.

It has already been shown in fluorobenzene that the bathochromic effect due to the greater polarisability of the C—F electrons towards the carbon atom as compared with that of the C—H electrons masks completely the displacement (in the case of fluorobenzene to shorter wavelengths) to be expected from the "polarity" factor mentioned. This should be true, to an even greater degree, for all other investigated substituents, since they contain much more strongly polarisable electronic systems.

The observed displacements of the benzene K-band to longer wavelengths indicate that the electronic polarisability towards the phenyl group increases in the order $C—H < C—F$ (D, 48 Å in hexane; 38 Å in ethanol) $< C—OH$ (98 Å; 160 Å) $< C—OMe$ (178 Å; 165 Å) $< C—NH_2$ (320 Å; 314 Å) $< C—O^-$ (—; 344 Å) $< C—SH$ (346 Å; 345 Å) $< C—SMe$ (511 Å; 510 Å $< C—S^-$ (—; 650 Å).

Qualitatively, this order coincides in the case of $C—F < C—OH < C—NH_2$ and of $C—OH < C—SH$ with the position of the atoms in the periodic table, i.e. the increasing electron repelling (decreasing electron attracting) character of the substituents. However, the electronic polarisability of the C—F, C—OH and C—OMe groups and of the C—SH and C—SMe groups is appreciably greater than that of the more strongly electron repelling C—H group and C—NH_2 and C—O^- groups respectively.

The observation that the K-band of thiophenol appears at only slightly longer wavelengths (2375 Å in ethanol) than the K-band of aniline (2344 Å) and that its position is similar to that of the phenoxide ion (2374 Å) is accounted for by a moderate, but greater contribution to the band displacements from the electron shift in the phenyl group (on substitution by the more strongly electron repelling NH_2 and O^- substituents) in the latter molecules (cf. also below).

*Hydrogen bond formation.* The K-bands of the phenoxide and the thiophenoxide ions are displaced to shorter wavelengths on replacing ethanol by water as solvent (29 and 60 Å respectively). All p-halogeno-phenoxide ions[3] and, as will be shown below, the p-methoxy-, p-amino-, and p-methylmercapto derivatives behave similarly (for data, cf. Table 3). This effect is due to the formation of stronger, and possibly multiple, hydrogen bonds of the charged atoms with water and the resulting reduction of both their electron repelling character and the polarisability of their unshared electrons. This change corresponds to the much greater one observed in the extreme case of proton addition, i.e. on formation of a hydroxyl or thiol group respectively. A systematic investigation of this matter will be reported elsewhere.

On the other hand, the appreciable displacement of the K-band of phenol to

*longer* wavelengths on replacing hexane by ethanol as solvent (72 Å) is, as already shown for many phenol derivatives,[6] due to hydrogen bond formation between the phenolic hydrogen atom and the oxygen atom of ethanol. This is responsible for an increase of the electron repelling character of the hydroxyl group as well as of the polarisability of the OH . . . OHEt electronic system. Again, this effect is qualitatively similar to the much greater one in the extreme case of complete ionisation, i.e. formation of the phenoxide ion.

No significant band displacement is observed for thiophenol indicating that the thiol group forms only a very weak, or no hydrogen bond with ethanol.

### (b) p-*Nitrobenzene derivatives*

Data for the maxima of the K-bands of the *p*-nitrobenzene derivatives (V), the displacements of the maxima on introduction of the substituents(X), and the *differences* of the displacements observed in the benzene series and the *p*-nitrobenzene series (D*) are shown in the second column of Table 1. The effective electron migration corresponding to the K-band transition is always directed, as in the benzene derivatives, towards the phenyl group: This is indicated in (V) by a long arrow.

$$\overset{\longleftarrow}{\underset{V}{p\text{-}O_2N\text{—}C_6H_4\text{—}X}}$$
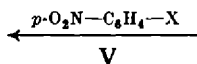
Except for *p*-nitrofluorobenzene, the displacements of the K-bands to longer wavelengths on introduction of the investigated substituents (V, X = OH, OMe, SH, SMe, $NH_2$, $O^-$, $S^-$) into nitrobenzene are considerably greater than those observed in the benzene series, the differences (D*) being enhanced on replacing hexane by ethanol.

This is accounted for by two (artificially separated) effects. (1) The increased effective nuclear charge (election deficiency) at the carbon atoms on introduction of the nitro-group, which is greater in ethanol than in hexane, is responsible for electron shifts in the terminal groups C—X (accompanied by changes of the interatomic distances and bond energies) and, thus, for an increase of their electron polarisability towards the carbon atom. As already shown,[3,7] these shifts involve an inductive mechanism and not a delocalisation of the orbitals of the unshared electrons (mesomeric effect). (2) The increased electron repelling character of the substituents (in turn) causes greater electron shifts in the substituted phenyl group. This, together with the even more important *additional* electron shifts within the C—$NO_2$ group, will result in a much greater increase of the electronic polarisability of the substituted nitrophenyl system as compared with that of the phenyl group in the corresponding benzene derivatives.

In contrast to all other substituents, which can be assumed to be electron repelling in the nitrobenzene series, the bathochromic effect due to the electron shift towards the carbon atom within the C—F bond on introduction of the nitro group is balanced by a hypsochromic effect due to the electron shift in the opposite direction within

[6] R. A. Morton and L. A. Stubbs, *J. Chem. Soc.* 1347 (1940); A. Burawoy and J. T. Chamberlain, *J. Chem Soc.* 2310, 3734 (1952); A. Burawoy, *Proceedings of the International Symposium on Hydrogen Bonding.* In press.

[7] A. Burawoy, *Trans. Faraday Soc.* **40**, 537 (1944); *Disc. Faraday Soc.* **10**, 104 (1951); *Chem. & Ind.* **63**, 434 (1944); *Contribution to the Study of Molecular Structure* p. 73. Desoer, Liège (1947–1948); A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954).

TABLE 1. MAXIMA OF K-BANDS IN Å

| X | Solvent | | $C_6H_5$—X $\leftarrow$ | $p\text{-}O_2N$—$C_6H_4$—X $\leftarrow$ | $p\text{-}H_3\overset{+}{N}$—$C_6H_4$—X $\leftarrow$ |
|---|---|---|---|---|---|
| H | EtOH | $\lambda$ | ~2030[a] | 2595[a] | ~2025[a] |
| | | $\varepsilon$ | — | 9500 | — |
| | $C_6H_{14}$ | $\lambda$ | 2020[b] | 2513[a] | — |
| | | $\varepsilon$ | 6600 | 9000 | |
| | $H_2O$ | $\lambda$ | 2035[a] | 2685[a] | 2030[a] |
| | | $\varepsilon$ | 7400 | 7800 | 7500 |
| F[3] | EtOH | $\lambda$ | 2068 | 2622 | 2078 |
| | | $\varepsilon$ | 3000 | 9000 | 3400 |
| | | D | +38 | +27 | +53 |
| | | D* | — | −11 | +15 |
| | $C_6H_{14}$ | $\lambda$ | 2068 | 2569 | — |
| | | $\varepsilon$ | 3000 | 8200 | |
| | | D | +48 | +56 | |
| | | D* | — | +8 | |
| HO | EtOH | $\lambda$ | 2190 | 3140 | 2223 |
| | | $\varepsilon$ | 5500 | 13,000 | 8000 |
| | | D | −160 | +545 | +198 |
| | | D* | — | +385 | +38 |
| | $C_6H_{14}$ | $\lambda$ | 2118 | 2870 | — |
| | | $\varepsilon$ | 5500 | 12,000 | |
| | | D | +98 | +357 | |
| | | D* | — | +265 | |
| MeO | EtOH | $\lambda$ | 2195[a] | 3050 | 2223 |
| | | $\varepsilon$ | 7500 | 13,800 | 8000 |
| | | D | +165 | +455 | +198 |
| | | D* | — | +290 | +33 |
| | $C_6H_{14}$ | $\lambda$ | 2198[a] | 2920 | — |
| | | $\varepsilon$ | 7000 | 13,500 | |
| | | D | +178 | −407 | |
| | | D* | — | +229 | |
| HS | EtOH | $\lambda$ | 2375 | 3175 | 2425 |
| | | $\varepsilon$ | 8800 | 12,000 | 11,000 |
| | | D | +345 | +580 | +403 |
| | | D* | — | +235 | +58 |
| | $C_6H_{14}$ | $\lambda$ | 2366 | 3035 | — |
| | | $\varepsilon$ | 7400 | 14,000 | |
| | | D | +346 | +522 | |
| | | D* | — | +176 | |
| MeS | EtOH | $\lambda$ | 2531 | 3408[b] | 2560[c] |
| | | $\varepsilon$ | 10,000 | 14,000 | 14,000 |
| | | D | +501 | +813 | +535 |
| | | D* | — | +312 | +34 |
| | $C_6H_{14}$ | $\lambda$ | 2531[d] | 3248 | — |
| | | $\varepsilon$ | 9000 | 15,000 | |
| | | D | +511 | +735 | |
| | | D* | — | +224 | |
| $H_2N$ | EtOH | $\lambda$ | 2344[a] | 3725 | 2444 |
| | | $\varepsilon$ | 8000 | 16,800 | 10,000 |
| | | D | +314 | +1130 | +419 |
| | | D* | — | +816 | +105 |

[8] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.* **69**, 2714 (1947).
[9] J. R. Platt and H. B. Klevens, *Tech. Rept.* 1953–1954, Part I. Office of Naval Research.

TABLE 1—*Continued*

| X | Solvent | $C_6H_5$—X $\leftarrow$ | | $p\text{-}O_2N\text{-}C_6H_4\text{-}X$ $\leftarrow$ | $p\text{-}\overset{+}{H_3}N\text{-}C_6H_4\text{-}X$ $\leftarrow$ |
|---|---------|---|---|---|---|
| O⁻ | $C_6H_{14}$ | $\lambda$ | 2340ᵃ | 3203 | — |
| | | $\varepsilon$ | 7500 | 14,000 | |
| | | D | +320 | +690 | |
| | | D* | — | +370 | |
| | EtOH | $\lambda$ | 2374ᵃ | 4010 | — |
| | | $\varepsilon$ | 12,500 | 24,000 | |
| | | D | +344 | +1415 | |
| | | D* | — | +1071 | |
| | $H_2O$ | $\lambda$ | 2345³,ᵈ | 3990ᶠ | — |
| | | $\varepsilon$ | 11,000 | 19,000 | |
| | | D | +310 | +1305 | |
| | | D* | — | +995 | |
| S⁻ | EtOH | $\lambda$ | 2680 | 4210 | — |
| | | $\varepsilon$ | 14,500 | 15,000 | |
| | | D | +650 | +1615 | |
| | | D* | — | +965 | |
| | $H_2O$ | $\lambda$ | 2620 | 4075 | — |
| | | $\varepsilon$ | 12,500 | 12,000 | |
| | | D | +585 | +1390 | |
| | | D* | — | +805 | |

D* Increase of displacement by the substituent X as compared with the displacement in the mono-substituted benzene derivatives.
ᵃ estimated. ᵇ Fehnel and Carmack[10] give 338 mμ. ᶜ Fehnel and Carmack[10] give 254 mμ in water. ᵈ Mangini and Passerini[11] give 254 mμ. ᵉ Doub and Vandenbelt[8] give 235 mμ. ᶠ Doub and Vandenbelt[8] give 402·5 mμ.

the $O_2N$—C system on introduction of the still electron attracting fluorine atom. The former effect is reduced in hexane (D* being only +8 Å) and even reversed in ethanol (D*, —11 Å), since the polarity and the electron attracting power of the C— F group is enhanced in the latter solvent.[3]

The given interpretation is convincingly supported by the fact that the *differences* in the displacements of the K-bands of benzene and nitrobenzene (D*) increase in the order of substituents F (8 Å in hexane; —11 Å in ethanol) ≪ SH (176 Å; 235 Å) < OMe (229 Å; 290 Å) ~ SMe (224 Å; 312 Å) < OH (265 Å; 385 Å) ≪ NH₂ (370 Å; 816 Å) < S⁻ (—; 965 Å) < O⁻ (—; 1071 Å), and that, again except for the fluorine atom (see above), this effect is enhanced in the same order of substituents on replacing hexane by ethanol.

This is in agreement with the general experience, based on well-known studies of physical properties and, in particular, of the rates of chemical reactions and of equilibria, that the electron shifts resulting from an increased electron demand at the carbon atom of a group C—X (in this case, on introduction of the nitro group and on replacement of hexane by ethanol) increase in the given order of substituents X which, except for the hydrogen atom, coincides, on the whole, with their electron repelling character.*

It should be noted, however, that a more quantitative analysis of the differences

* This is commonly attributed to an increasing mesomeric effect in the order given.
[10] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.* **71**, 2889 (1949).
[11] A. Mangini and R. Passerini, *J. Chem. Soc.* 4954 (1956).

D* would require the consideration of an additional factor which will be discussed in greater detail elsewhere. The degree of stabilisation of the normal excited state, i.e. the red-shift of a K-band, due to the perturbation not only, as is well-known, by a terminal —CH=CH$_2$ group, but by *any* substituent decreases as the length (or polarisability) of the substituted absorbing system increases. This factor will tend to reduce the greater bathochromic effect of substituents in the *p*-nitrobenzene derivatives as compared with their effect in the benzene derivatives, i.e. the displacements D*. This factor cannot be neglected in an analysis of the significance of the only moderate differences of D* observed for the sulphur and corresponding oxygen containing substituents, for which reason it is not attempted at this stage.

The preceding discussion shows that in the *p*-nitrobenzene derivatives the polarisability of the terminal groups C—X as well as of the substituted system becomes much more closely related to the electron repelling character of the substituents than in the benzene series. This is particularly well illustrated by the observation (1) that, in contrast to the very similar positions of the K-bands of thiophenol, aniline and the phenoxide ion in ethanolic solution (2374 Å; 2344 Å; 2375 Å), those of the corresponding *p*-nitrobenzene derivatives are strongly displaced from 3175 Å to 3725 Å and 4010 Å, i.e. in their order of polarity, and (2) that, whereas thioanisole absorbs at considerably longer wavelengths (2531 Å in ethanol and hexane) than the more polar aniline (2340; 2344 Å), in hexane the difference is considerably reduced for *p*-nitrothioanisole (3248 Å) and *p*-nitroaniline (3203 Å) and in ethanol the latter absorbs even at much longer wavelengths (3725 Å) than the former (3408 Å).

*Effect of hydrogen bond formation.* The displacements to shorter wavelengths of the K-bands of the phenoxide and thiophenoxide ions on replacing ethanol by the more strongly hydrogen bonding water (29 and 60 Å respectively) are also observed for the corresponding *p*-nitrobenzene derivatives (110 and 225 Å respectively). They are greater, because they include the effect arising from the reduced polarity of the O$_2$N—C system.

Similarly the contribution of the now increased polarity of the O$_2$N—C group explains that the displacement of the K-band of *p*-nitrophenol to longer wavelengths due to hydrogen bond formation of the phenolic hydrogen atom with ethanol is greater than that observed for phenol. Whereas in hexane the K-band of *p*-nitroanisole appears at longer wavelengths (by 50 Å) than that of *p*-nitrophenol, in ethanol the reverse is true, the K-band of nitrophenol absorbing at much longer wavelengths (by 90 Å). Thus, the displacement caused by hydrogen bond formation is approximately 140 Å as compared with the 75 Å observed for phenol itself.

Again, the spectrum of *p*-nitrothiophenol in ethanol does not indicate the formation of a hydrogen bond, since the difference between the position of the K-bands of this thiophenol and its methyl ether is even slightly greater in ethanol (233 Å) than in hexane (213 Å). The different tendency of the hydroxyl and thiol groups to form hydrogen bonds accounts for the observation that in ethanol the positions of the K-bands of *p*-nitrophenol and *p*-nitrothiophenol are similar (3140 and 3175 Å respectively), but in hexane are very different (2870 and 3035 Å respectively).

(c) p-*Substituted anilinium ions*

According to Doub and Vandenbelt[8] the maxima of the K-bands of benzene and of the anilinium ion in water appear at 2035 Å and 2030 Å, respectively. The

insignificant displacement to shorter wavelengths on introduction of the $\overset{+}{N}H_3$ group indicates that the electron polarisability of the C—$\overset{+}{N}H_3$ group, similar to that of the C—F group, at least towards the substituent is smaller than that of the C—H bond. Assuming the direction of the effective charge migration is towards the ammonium group (VI), the electron shift (in the ground state) within the phenyl group should have produced a slight displacement of the K-band to longer wavelengths.

$$\text{X—C}_6\text{H}_4\text{—}\overset{+}{N}\text{H}_3 \xrightarrow{\quad\quad} \quad (\text{X} = \text{H, F, OH, OMe, SH, SMe, NH}_2)$$
$$\text{VI}$$
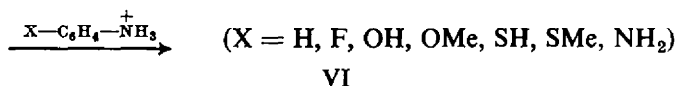
As shown in the third column of Table 1, the introduction of the $\overset{+}{N}H_3$ group into the *para* position of fluorobenzene, phenol, anisole, thiophenol, thioanisole and aniline (VI) displaces the corresponding K-bands moderately to longer wavelengths (D*: 15, 38, 33, 58, 34, 105 Å). This can be attributed to an increased electron shift, particularly within the C—X groups, towards the carbon atom, this shift, as could be expected, being greater than that occurring in the corresponding C—H bond of the anilinium ion itself.

The *increase* of the displacements of the benzene K-band by the OH, OMe, SH, SMe and NH$_2$ substituents on introduction of the $\overset{+}{N}H_3$ group is much smaller than that observed in the corresponding *p*-nitrobenzene derivatives, which should be attributed to much smaller electron shifts in the $\overset{+}{H_3N}$—C system than in the O$_2$N—C system. In agreement with this interpretation, the smaller displacement of the K-band of nitrobenzene as compared with that of benzene on introduction of the electron attracting fluorine atom (D*, —11 Å in ethanol) due to the reduced polarity of the O$_2$N—C group (cf. above) is not observed in the *p*-fluoroanilinium ion (D*, +15 Å).

### 3. EFFECT AS ELECTRON-ACCEPTING TERMINAL GROUPS OF THE EFFECTIVE ELECTRON MIGRATION

As recently shown,[3] the electronic polarisability of the (aromatic) C—Hal groups is greater towards the carbon atom than in the opposite direction.* Thus, these groups are responsible for much smaller displacements of the K-bands to longer wavelengths and in the case of the C—F group even for displacements to shorter wavelengths, if they are electron-receiving terminal groups of the effective electron migration, e.g. in absorbing systems such as (VII). This is illustrated in Table 2 by a

TABLE 2. DISPLACEMENTS OF K-BANDS (IN Å) IN HEXANE SOLUTION ON
INTRODUCTION OF HALOGEN ATOMS

| X | $\text{X—C}_6\text{H}_5 \xrightarrow{}$ | $p\text{-X—C}_6\text{H}_4\text{—NH}_2 \xleftarrow{}$ | $p\text{-X—C}_6\text{H}_4\text{—OMe} \xleftarrow{}$ | $p\text{-X—C}_6\text{H}_4\text{—I} \xleftarrow{}$ |
|---|---|---|---|---|
| F | 48 | —35 | —35 | —13 |
| Cl | 132 | 73 | 82 | 63 |
| Br | 140 | 78 | 72 | 90 |
| I | 280 | 123 | 142 | 125 |

* This is in contrast to the reversed order of polarisability in the aliphatic C—Hal groups.[4]

comparison of the displacements observed for the K-bands of the halogenobenzenes with those e.g. observed for the *p*-halogenoanilines, *p*-halogenoanisoles and *p*-halogenoiodobenzenes in hexane solution.

$$\xrightarrow{p\text{-A}—C_6H_4—Hal} \quad (A = NH_2, OMe, I)$$
$$VII$$
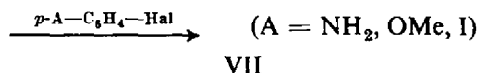
The effect of the hydroxyl, methoxyl, mercapto, methylmercapto, amino, and charged oxygen substituents at the receiving end of the effective electron migration (VIII) has now been investigated.

$$\xrightarrow{p\text{-A}—C_6H_4—X} \quad (X = OH, OMe, SH, SMe, NH_2, or O^-)$$
$$VIII$$
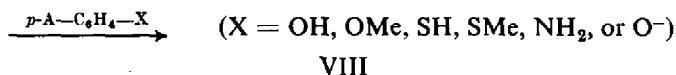
The observed maxima of the K-bands of thiophenol, thioanisole, and aniline in hexane and ethanol and of the phenoxide and thiophenoxide ions in ethanol and water (VIII, A = SH, SMe, NH_2, O^- or S^-) as well as their derivatives substituted in *para* position by similar groups (VIII, X) are collected in Table 3. The data have been arranged to show the effect of these substituents at the receiving end of the effective electron migration (the direction of which is indicated by long arrows). The corresponding displacements (D) are also given. A few data illustrating the effect of the fluorine atom, reported earlier,[3] are again added for comparison.

The direction of the effective electron migration corresponding to the observed K-band in these *p*-disubstituted benzene derivatives can be established by a comparative analysis of the displacements of the K-bands on introduction of the various groups (for the corresponding analysis applied to the *p*-substituted halogenobenzenes, cf. reference 3). Thus, the magnitude of the displacements due to an SMe group at the receiving end is 212–214 Å and 194–204 Å in the unambiguous cases of *p*:*p'*-dimethylmercapto-benzene and of the *p*-methylmercapto-thiophenoxide ion respectively. In contrast, the displacements of the K-bands of phenol, thiophenol, anisole, aniline, and the phenoxide ion on introduction of a methylmercapto group into the *p*-position vary between 253 and 452 Å, i.e. the K-band appears at much longer wavelengths than could be expected, if the SMe group would be at the receiving end of the electron migration of the transition.

Similarly, the displacement of the K-band due to the electron accepting terminal amino group in *p*-phenylenediamine, *p*-amino-thioanisole, the *p*-aminophenoxide and *p*-aminothiophenoxide ions varies between 22 and 119 Å, whereas the corresponding displacements in *p*-aminophenol, *p*-aminoanisole, and *p*-aminothiophenol (144–232 Å) are too high for a receiving terminal amino group.

Again, the differences between the position of the K-bands of *p*-hydroxythioanisole, of *p*-hydroxyaniline, and of *p*-hydroxythiophenol and that of the corresponding *p*-methoxy derivatives are small and are of the same order in both hexane and ethanol. The displacements to longer wavelengths due to hydrogen bond formation with ethanol to be expected for phenols, in which the hydroxyl groups are at the electron donating end of the effective electron migration, are not observed. Thus, the hydroxyl and methoxyl groups in these molecules can only be at the receiving end of the effective charge migration.

In Table 4, the observed displacements of the K-bands by the investigated groups at the donating and at the receiving ends respectively of the effective electron migration

TABLE 3. MAXIMA OF K-BANDS OF COMPOUNDS $p-A-C_6H_4-X$ IN Å

| X | Solvent | | A: MeS- | H₂N- | HS- | Me₂N- | S⁻- | O⁻- |
|---|---|---|---|---|---|---|---|---|
| H | EtOH | λ | 2531 | 2344 | 2375 | — | 2680 | 2374 |
| | | ε | 10,000 | 8000 | 8800 | | 14,500 | 12,500 |
| | C₆H₁₄ | λ | 2531 | 2340 | 2366 | 2500[11,a] | — | — |
| | | ε | 9000 | 7500 | 7400 | 14,100 | | |
| | H₂O | λ | 2487 | — | — | 2440[12] | 2620 | 2345 |
| | | ε | 10,000 | | | 8700 | 12,500 | 11,000 |
| F³ | EtOH | λ | — | 2334 | — | — | — | 2350 |
| | | ε | | 7000 | | | | 7500 |
| | | D | | −10 | | | | −24 |
| | C₆H₁₄ | λ | — | 2305 | — | — | — | — |
| | | ε | | 7000 | | | | |
| | | D | | −35 | | | | |
| | H₂O | λ | — | — | | | | 2318 |
| | | ε | | | | | | 6000 |
| | | D | | | | | | −27 |
| HO | EtOH | λ | 2552[b] | 2349 | 2375 | — | — | — |
| | | ε | 11,000 | 9300 | 8500 | | | |
| | | D | +21 | +5 | 0 | | | |
| | C₆H₁₄ | λ | 2570 | 2350 | 2346 | 2470[11,c] | — | — |
| | | ε | 7000 | 8000 | 8000 | 11 000 | | |
| | | D | +39 | +10 | −20 | −30 | | |
| MeO | EtOH | λ | 2560 | 2354 | 2396 | — | 2665 | 2390 |
| | | ε | 10,000 | 10,500 | 10,500 | | 16,000 | 8500 |
| | | D | +29 | +10 | +21 | | −15 | +16 |
| | C₆H₁₄ | λ | 2568 | 2370 | 2368 | 2500[11,c] | — | — |
| | | ε | 9000 | 10,000 | 9500 | 13,500 | | |
| | | D | +37 | +30 | +2 | 0 | | |
| | H₂O | λ | — | — | — | — | 2620 | 2352 |
| | | ε | | | | | 14,000 | 8500 |
| | | D | | | | | 0 | +7 |
| HS | EtOH | λ | 2695 | 2520 | — | — | — | — |
| | | ε | 15,000 | 14,000 | | | | |
| | | D | +164 | +176 | | | | |
| | C₆H₁₄ | λ | 2695 | 2510 | — | — | — | — |
| | | ε | 14,500 | 14,000 | | | | |
| | | D | +164 | +170 | | | | |
| H₂N | EtOH | λ | 2632[d] | 2440 | — | — | 2702 | 2452 |
| | | ε | 14,000 | 11,000 | | | 16,000 | 11,000 |
| | | D | +101 | +96 | | | +22 | +78 |
| | C₆H₁₄ | λ | 2632[e] | 2459 | — | 2560[11,c] | — | — |
| | | ε | 10,000 | 8500 | | 12,000 | | |
| | | D | +101 | +119 | | +60 | | |
| | H₂O | λ | — | — | — | — | 2657 | 2430 |
| | | ε | | | | | 15,000 | 10,500 |
| | | D | | | | | +37 | +85 |
| MeS | EtOH | λ | 2745 | — | — | — | 2874 | — |
| | | ε | 19,500 | | | | 17,500 | |
| | | D | +214 | | | | +194 | |
| | C₆H₁₄ | λ | 2743 | — | — | — | — | — |
| | | ε | 19,000 | | | | | |
| | | D | +212 | | | | | |

[12] H. E. Ungnade, J. Amer. Chem. Soc. 75, 432 (1953).

TABLE 3—*continued*

| X | Solvent | | A: MeS- | H₂N- | HS- | Me₂N- | S⁻- | O⁻- |
|---|---------|---|---------|------|-----|-------|-----|-----|
| O⁻ | H₂O | $\lambda$ | — | — | — | — | 2824 | — |
| | | $\varepsilon$ | | | | | 17,000 | |
| | | D | | | | | +204 | |
| | EtOH | $\lambda$ | 2627[f] | — | — | — | — | — |
| | | $\varepsilon$ | 14,500 | | | | | |
| | | D | +96 | | | | | |
| | H₂O | $\lambda$ | 2595[g] | — | — | 2450[11] | 2630 | 2402 |
| | | $\varepsilon$ | 15,000 | | | 11,500 | 13,000 | 8500 |
| | | D | +108 | | | ÷10 | +10 | ÷57 |

[a] Solvent, heptane. [b] Fehnel and Carmack[10] give 256 m$\mu$. [c] Solvent, cyclohexane. [d] Fehnel and Carmack[10] give 264 m$\mu$. [e] Mangini and Passerini[11] give 264 m$\mu$. [f] Fehnel and Carmack[10] give 263 m$\mu$. [g] Mangini and Passerini[11] give 259 m$\mu$.

are summarised. They show that, as in the case of the C—Hal groups, the electronic polarisability of the (aromatic) C—OH, C—OMe, C—SH, C—SMe, C—NH₂, and C—O⁻ groups is much greater towards the carbon atom than in the opposite direction. These groups are responsible for much smaller bathochromic displacements of the K-bands, if they are on the receiving end of the effective charge migration.

Also, it may be noted that the electronic polarisability of the investigated groups C—X increases approximately in the same order of substituents X in both directions. F < OH < OMe < NH₂ < O⁻ < SH < SMe. The displacements of the K-bands by the SH, NH₂, and O⁻ substituents as donating terminal groups are very similar (345, 314 and 344 Å respectively, in ethanol), because the electron repelling NH₂ and O⁻ substituents are responsible for electron shifts in the ground state of the substituted

TABLE 4. DISPLACEMENTS OF THE K-BANDS (IN Å) BY SUBSTITUENTS X

| X | X—C₆H₅ ⟵ | | (A = SH, SMe, NH₂ O⁻ or·S⁻) X—C₆H₄—A ⟵ | |
|---|------|--------|---------------|--------|
| | EtOH | C₆H₁₄ | EtOH or H₂O | C₆H₁₄ |
| F | 38 | 48 | −10/−27 | −17/−38 |
| HO | 160 | 92 | 0/27 | −20/39 |
| MeO | 165 | 178 | −15/29 | 2/37 |
| H₂N | 314 | 320 | 22/101 | 101/119 |
| O⁻ | 344 | — | 10/96 | — |
| HS | 345 | 346 | 164/176 | 164/170 |
| MeS | 501 | 511 | 194/214 | 212 |

phenyl group which coincide with the direction of the effective charge migration of the transition and, thus, make some additional contribution to the bathochromic displacement of the K-band (cf. above). On the other hand, when these groups are on the receiving end, the observed displacements of the K-bands are much smaller for the charged oxygen atom (10–96 Å) and for the amino group (22–101 Å) than for the

mercapto group (164–176 Å) since the electron repelling $O^-$ and $NH_2$ are now responsible for electron shifts (in the ground state) in the opposite direction to the effective charge migration.

The slight variations of the effect of the investigated groups at the receiving end of the effective charge migration on the position of the K-bands observed in different compounds may arise (1) from the small variations of the polarity of the absorbing systems and, in particular, of the terminal groups, (2) from changes in the degree of perturbation due to differences in the length (or polarisability) of the substituted systems (cf. above), and (3) from small, but varying contributions of the "complementary" charge migration of the transition in the only slightly polar molecules discussed. A detailed analysis and separation of these effects could only be speculative, and it is not attempted.

Table 3 shows also data reported by Ungnade[12] and by Mangini and Passerini[11] for the K-bands of dimethylaniline and of its derivatives containing in the para position a hydroxyl, methoxyl, amino and charged oxygen substituent respectively (IX). The displacements (D) by these substituents (at the receiving end of the effective electron migration of the transition) are, in agreement with those observed in the examples investigated by us, −30, 0, +60 and +10 Å respectively.

$$p\text{—}Me_2N\text{—}C_6H_4\text{—}X \longrightarrow \quad (X = OH, OMe, NH_2, O^-)$$

IX
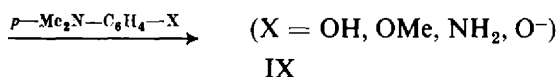
## 4. GENERAL CONCLUSIONS

The present investigation confirms the earlier conclusions summarised in the introduction of this paper. Organic molecules are built up of localised bonds only. The constitutive changes of covalent bonds, e.g. the variations of bond energies, interatomic distances and dipole moments, originate in changes of electron repulsions (effective nuclear charges) and involve inductive electron displacements only.

The normal excited state corresponding to a K-band can be described as a "hybrid" of interacting unperturbed states each involving one excited electron, the combined "unperturbed" state involving each electron pair being, for convenience, expressed by one arrow in formula (X). Here, each arrow also indicates the direction of the electron migration (on one side of the nodal plane formed) in phase with the effective charge migration of the observed transition. It should be noted that the total charge migration in this excited state will require the consideration of the "complementary" charge migration as expressed by (XI), but the observed transition energy (position of the K-band) is only to a negligible degree affected by the latter.

Although outside the scope of this paper, the electron migration in the branching electrons of the C—H bonds and (in brackets) the, in absence of any direct experimental evidence, only probable one in the branching non-bonding electrons of the substituents A and B are also indicated (for a general discussion of this matter, cf. reference 4).

The K-band is displaced to longer wavelengths by any structural change which increases the polarisability of the electrons in the absorbing system, i.e. the stability of the corresponding unperturbed excited states, e.g. by a replacement of a bond or group by a more strongly polarisable one or by electron shifts in the ground state coinciding with the effective electron migration of the transition.

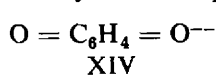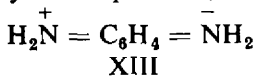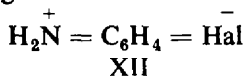X                                                    XI
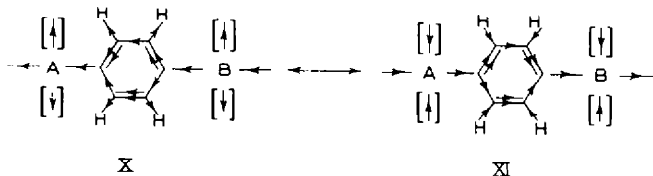
The wave-mechanical resonance characteristic for the electronic perturbations in the excited state of polyelectronic systems represents a physical phenomenon which is absent in the ground state.[4] Thus, the introduction of a substituent possessing an electron affinity similar to the hydrogen atom, e.g. the OMe, SMe, (vinyl or phenyl*) groups in anisole, thioanisole, (styrene or diphenyl) respectively, will be responsible in the *ground state* for only a *negligible* change in the electronic system of the substituted phenyl group, but displace the K-band *strongly* to longer wavelengths as a result of the increased perturbation by the electronic system of the substituent in the *excited state*.

The widely accepted and varying theoretical interpretations of electronic spectra (based on molecular structures involving simplifying concepts such as non-localised bonds, mesomeric electron displacements, a consideration of $\pi$ electrons only and, in particular, the attempt to build up electronic structures "vertically" with the help of many-centred molecular orbitals by analogy to the building-up principle of atomic structures), again, do not allow for a consistent explanation of the data discussed in this paper.

There is, certainly, no relationship between the (assumed) mesomeric (resonance or delocalisation) effect of the substituents in the ground state particularly of the mono-substituted benzene derivatives and the displacements of the corresponding K-bands to longer wavelengths. As known from studies of physical properties, rates of chemical reactions and chemical equilibria, the former effect, if real, would increase in the order $Me_3C < H_3C < I < Br < Cl < F < SH(SMe) < OH(OMe) < NH_2$, whereas the K-band of benzene is displaced to longer wavelengths (in hexane) in the order $H_3C < F, CMe_3 < OH < Cl < Br < OMe < I < NH_2 < SH < SMe$.

What should be even more important, it is difficult to see how any of the theoretical systems involving bond delocalisation can account for the effect of the investigated groups at *the receiving end* of the effective charge migration, e.g. for the much smaller bathochromic and in the case of C—F and, often, of C—OH the hypsochromic band displacements, for the increase of the band displacements in almost the same order of substituents at both the donating and receiving ends of the electron migration (see Table 4), or even for the participation of these groups in the electron migration of the transition. Expressed in valence-bond terminology, contributions from states such as (XII, XIII or XIV) which would contain ten electrons at the halogen, nitrogen or oxygen atoms cannot be seriously contemplated. (cf. also Burawoy and Thompson.[3])

$$\overset{+}{H_2N} = C_6H_4 = \overset{-}{Hal} \qquad \overset{+}{H_2N} = C_6H_4 = \overset{-}{NH_2} \qquad O = C_6H_4 = O^{--}$$

XII                          XIII                          XIV

## 5. 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

* The effect of terminal groups containing multiple bonds on K-bands will be discussed in the next part of this series (*Tetrahedron*, in press).

being employed as the source of light. They were in many cases checked with a Hilger Uvispek Photoelectric Spectrophotometer. The spectra of phenol, the $p$-nitropheno-late ion and the $p$-nitrothiophenolate ion were measured by the latter method. Those of the anilinium ions were determined in ethanol and concentrated hydrochloric acid (99 : 1), except for the $p$-aminoanilinium ion the spectrum of which was obtained with a 0·001 M solution of $p$-phenylenediamine in ethanol and 0·4 N aqueous hydrochloric acid (99 : 1). All phenoxide and thiophenoxide ions were measured in 0·3 per cent ethanolic sodium ethoxide and 0·1 N aqueous sodium hydroxide respectively, those of the air-sensitive dibasic salts of hydroquinone and thiohydroquinone in 0·1 N aqueous sodium hydroxide containing 0·1 per cent of sodium bisulphite.

Great care has been taken to obtain the investigated compounds in a high state of purity. All mercaptans were also analysed. Dithiohydroquinone monomethylether has not been previously described.

*Dithiohydroquinone monomethylether*. $p$-Aminothioanisole (27·8 g) was diazotised by the addition of sodium nitrite (15·5 g), 10 per cent of hydrochloric acid (75 cm³) and sufficient sodium acetate to buffer the solution. The diazonium salt solution was added slowly with vigorous stirring to a solution of potassium ethylxanthate (60 g) in water (40 cm³) kept at 70/80°. Stirring was continued at this temperature for another hour.

The resulting dark-coloured oil was separated and refluxed with potassium hydroxide (23 g), glucose (23 g) and ethanol (400 cm³) for 3 hr. The solution was concentrated to 60 cm³, acidified with dilute sulphuric acid, and the thiol, after addition of zinc dust (3·0 g), steam-distilled. The distillate was extracted with ether, the ether removed after drying over anhydrous sodium sulphate, and the thiol frac-tionated under reduced pressure, b.p. 116/117°/3 mm, m.p. 29–30°. Yield: 24 g; 80 per cent of theory. (Found: C, 53·8; H, 5·1; S, 41·1. Calc. for $C_7H_8S_2$ C, 54·1; H, 5·2; S, 40·9 per cent).

*Dithiohydroquinone dimethylether*. A solution of the monomethylether of dithio-hydroquinone (10 g) in 40 per cent of aqueous sodium hydroxide (20 cm³) was vigour-ously stirred while dimethylsulphate (5·0 g) was added. The precipitate of the dimethylether was collected (9·0 g; 83 per cent of theory). It crystallised from light petroleum (b.p. 60–80°) as colourless plates of m.p. 85° (Zincke and Frohneberg[13] obtained it from dithiohydroquinone and give m.p. 85°) (Found; C, 56·4; H, 5·9; S, 37·4. $C_8H_{10}S_2$ requires C, 56·5; H, 5·9; S, 37·6 per cent).

[13] Th. Zincke and W. Frohneberg, *Ber. Dtsch. Chem. Ges.* **42**, 2721 (1909).