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ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—VI[*]

THE ELECTRONIC SPECTRA OF *p*-TERPHENYL AND ITS DERIVATES

P. BROCKLEHURST,[†] the late A. BURAWOY and A. R. THOMPSON
Manchester College of Science and Technology

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Abstract- This investigation deals with the effect of *para*-substituents on the positions observed in the high intensity bands (K-bands) of a *p*-polyphenyl series as the length of the conjugated system increases. The results obtained are interpreted in terms of the polarity and polarizability of the absorbing system. It is implicit in the discussion that a vinyl, or phenyl group behaves in the same manner as any of the other simple groups discussed.

INTRODUCTION

THE effect of substituents on the position of the absorption bands in the spectra of organic compounds is of considerable complexity, since it is dependent upon the location of the substituent within the absorbing system. The K-bands are best understood. There is general agreement that qualitatively they are due to transitions involving an electronic migration along the axis of the absorbing conjugated system.[1] Burawoy and Spinner[2] have shown that the position of a K-band is determined by two factors:

1. *The polarity of the absorbing system*

Influences such as terminal groups that increase the polarity of the absorbing system in the ground state facilitate the electronic migration, stabilize the excited state, and displace the K-band to longer wavelengths.

2. *The polarizability of the absorbing system*

The more polarizable the electrons of a terminal group are, the greater will be the displacement of the K-band to longer wavelengths.

According to this view the red-shift of the K-bands with the increasing number of conjugated linkages has to be attributed to the replacement of terminal C—H bonds by the more polarizable C- C C group. It is known that this effect decreases with the increasing length of the absorbing conjugated system. If the terminal C—H group is replaced by any other substituent, i.e. a methyl group, chlorine atom or nitro group,

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[*] Part V: *Tetrahedron* 5, 340 (1959).

[†] Present address: Basic Research Department, Thomas Hedley, City Road, Newcastle upon Tyne, 1.

[1] R. S. Mulliken, *J. Chem. Phys.* 3, 522 (1935); 7, 14, 21, 121, 339, 357, 395 (1939); G. N. Lewis and M. Calvin, *Chem. Rev.* 25, 309 (1939); A. Burawoy, *Disc. Faraday Soc.* 9, 70 (1950).

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

etc. the bathochromic effect should decrease with increasing length of the substituted conjugated system. However, in the case of a terminal vinyl or phenyl group, the first factor, i.e. any change of polarity of the absorbing system, is of little or no importance, and could be expected to become apparent only in the case of other, more polar terminal groups.

It was, therefore, thought to be of interest to test this view by investigating the differing effect of such polar terminal groups on the position of the K-band as the length of the substituted conjugated system increases. A series of *p*-substituted *p*-terphenyl compounds have been prepared and their spectra in ethanol and hexane determined. The results have been compared with those obtained from the corresponding benzene and diphenyl derivatives. This data can be seen in Table 1.

DISCUSSION

(a) *The effect of groups containing multiple bonds*

The displacement (D) observed on introducing a vinyl or a phenyl group in the *para* position of (benzene), diphenyl, and *p*-terphenyl decreases in both the (benzene) and diphenyl derivatives from 420–450 Å to 280–300 Å and finally to 170 Å (as shown by the spectrum of *p*-quaterphenyl in hexane). In contrast the red-shift of the K-band in benzaldehyde and in *p*-phenyl-benzaldehyde remains almost unchanged; the decreasing contribution of the polarizability of the substituent is balanced by the enhanced polarity (and resultant polarizability) of the second phenyl group in *p*-phenyl-benzaldehyde as compared with diphenyl itself. This interpretation is supported by the fact that the latter contribution is smaller in hexane than in ethanol, since the polarity of the molecule is smaller in the less polar solvent.

N-Methyl-benzaldimide and *p*-phenyl-N-methyl-benzaldimide show an intermediate behaviour, since the electron attracting power of the —C=N—Me group is greater than that of a vinyl group, but smaller than that of a carbonyl group. The effect of the —C=N—Me group is now smaller in the diphenyl derivative, but the decrease is definitely smaller than that observed for the vinyl group.

The behaviour of the powerful electron attracting nitro and cyano groups is similar to that of the carbonyl group. The displacement of the K-band is greater for *p*-nitrodiphenyl (585 Å) and *p*-cyanodiphenyl (215 Å) than in the corresponding benzene derivatives (565 and 205 Å). This displacement falls appreciably in the *p*-terphenyl derivatives (491 and 136 Å), but this decrease is less pronounced than that observed for *p*-phenyl substituent (447 → 283 → 170 Å). This indicates some small contribution caused by the induced polarity of the third phenyl group in the substituted terphenyl residue, since the polarity of the third phenyl group is to a lesser degree enhanced than that of the less distant second one in the diphenyl derivative.

(b) *The effect of "auxochromic groups"* (—OH, —OMe, —NH_2, —$\overline{O}$)

In hexane solution, the methoxyl group has a stronger bathochromic effect than a hydroxyl group. In ethanol, however, both groups behave similarly. Morton and Stubbs[3] were the first to show that this is due to the formation of an external hydrogen bond between the hydroxyl group and ethanol, which conclusion has also been confirmed by Burawoy and Chamberlain.[4] On introduction of these substituents into the

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[3] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.* 901, 920 (1934); 1347 (1940).

[4] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.* 2310 (1952).

Table 1. Maxima of K-bands in Å

X	Solvent	X–Ph	D	X–Ph·Ph	D	X Ph·Ph·Ph	D
H	EtOH	2030[5]		2475[6] 19,500		2769 32,000	
	C_6H_{14}	2020[5] 6600		2467[6] 1900		2750 32,000	
C_6H_5	EtOH	2475[6] 19,500	+445	2769 32,000	+294		—
	C_6H_{14}	2467[6] 19,000	+447	2750 32,000	+283	2920[8] 55,000	+170
$H_2C{=}CH$—	EtOH	2453[7] 15,000	+423	2761 20,000	+286	—	—
	C_6H_{14}	2451[7] 11,000	+431	2755 19,500	+288	—	—
Me—N=CH—	EtOH	2450[7] 15,000	+420	2815 28,000	+340	–	
	C_6H_{14}	2420[7] 15,000	+400	2752 29,000	+285		—
O=CH	EtOH	2445[6] 13,500	+415	2895 23,000	+420		
	C_6H_{14}	2408[6] 1400	+388	2828 24,000	+361		
O_2N	EtOH	2595[6] 9500	+565	3060 18,000	+585	3260 21,000	+491
	C_6H_{14}	2513[6] 9000	+493	2935 18,000	+471	3150 26,000	+400
N≡C—	EtOH	2235[7] 13,000	+205	2690 28,500	+215	2905 19,000	+136
	C_6H_{14}	2222[7] 17,000	+192	2665 21,000	+198	2865 25,000	+115
HO-	EtOH	2190[6] 5500	+160	2612[8] 22,500	+137	2890 31,000	+121
	C_6H_{14}	2118[6] 5500	+98	2548[8] 25,000	+81	2810	+60

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[5] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.* 69, 2714 (1947).
[6] A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).
[7] A. Burawoy and J. P. Critchley, *Tetrahedron* 5, 340 (1959).
[8] A. E. Gillam and D. H. Hey, *J. Chem. Soc.* 364 (1941).

TABLE 1– *continued*

X	Solvent	X–Ph	D	X·Ph·Ph	D	X–Ph·Ph·Ph	D
MeO	EtOH	2195[a] 7500	+165	2610[a] 22,000	+135	2875 33,000	+106
	C_6H_{14}	2198[a] 7000	+178	2596[a] 27,000	+139	2854 34,000	+104
H_2N–	EtOH	2340[a] 8000	+314	2805 19,000	+330	3010 32,000	+241
	C_6H_{14}	2340[a] 7500	+320	2744 19,000	+277	2959 27,000	+209
O^-–	EtOH +0·1% NaOEt	2374[a] 12,500	+344	2970 23,000	+495	3270 33,000	+451
F–	EtOH	2068[a] 3000	+38	2462[a] 18,600	13	2764 32,000	5
	C_6H_{14}	2068[a] 3000	+48	2450[a] 16,000	17	2737 31,000	−13
Cl	EtOH	2130[a] 6100	+100	2550[a] 23,500	+75	2817 32,000	+48
	C_6H_{14}	2152[a] 9600	+132	2527[a] 20,500	+60	2782 34,000	+32
Br	EtOH	2135[a] 7300	+105	2562[a] 25,500	+87	2832 34,000	+63
	C_6H_{14}	2160[a] 7700	+140	2540[a] 22,000	+73	2790 36,000	+40
I–	EtOH	2275[a] 12,000	+245	2586[a] 25,500	+111	2843 36,000	+74
	C_6H_{14}	2300[a] 11,000	+280	2573[a] 22,000	+106	2805 33,000	+55
H_3C	EtOH	2065[a] 7000	30	2520[a] 21,000	+45	2810 29,000	+41
	C_6H_{14}	—	—	2513[5] 19,000	+46	2795 31,000	+45
H_3N^+	EtOH/ conc. HCl 99:1	2030[a] 7500	5	2483 19,000	+8	2800 33,000	+39

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[a] These figures were determined with *water* as solvent, by Doub and Vandenbelt[4] who also give 2035 Å as the maximum for benzene in that solvent.

D = Increase of displacement by the substituent X compared with parent hydrocarbon.

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

para position, the displacement of the K-bands of (benzene), diphenyl and *p*-terphenyl decreases in this order, but the overall percentage decrease is smaller than in the case of a vinyl group, which may indicate some contribution of the polarity factor. It is noteworthy that, although the position of the K-bands of both the phenols and the phenol ethers in ethanol is similar, the displacements fall off more appreciably in the case of the phenol ethers (165 → 135 → 106 Å) as compared with the phenols (160 → 137 → 121 Å). This effect can be explained on the basis of the electronic polarizability of the methoxyl group being greater than that of the hydrogen bonded hydroxyl group. This, in turn, is balanced by the greater electron repelling character of the latter group.

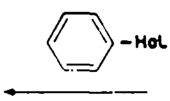
The amino group behaves similarly, but the greater electron repelling nature, and the resultant increased contribution of the polarity factor is shown by:

1. the greater red-shift in ethanol of the K-band of *p*-amino diphenyl (330 Å) compared with that of the K-band of aniline (314 Å).
2. the apparently more rapid fall of the displacement in the non-polar hexane (320 → 277 → 209 Å) than in the polar ethanol (314 → 330 → 241 Å).

The effect due to the increased polarity of the substituted system is convincingly demonstrated by the introduction of the powerful electron repelling negatively charged oxygen atom in the phenolate ions. The redshift is considerably greater in the *p*-phenyl-phenolate ion (495 Å) than in the phenolate ion itself (344 Å) and the displacement only slightly decreases in the ion of *p*-hydroxy-*p*-terphenyl (451 Å).

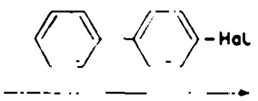
(c) *The effect of halogen atoms*

Burawoy and Thompson[6] have shown that the direction of the electron migration in the halogenobenzenes is towards the phenyl group (I):



This follows from the displacement of the K-bands to shorter wavelengths on replacing hexane by ethanol. The electron shift in the phenyl group due to the electron attracting terminal halogen atoms reduces the polarizability of the system away from the halogen atom, but this effect is masked by the opposing greater polarizability of the C—Hal electrons towards the carbon atoms (increasing in the order C—F < C—Cl < C—Br < C—I).

In contrast, the electron migration determining the stability of the excited state in the *p*-halogenodiphenyls is in the opposite direction (II) to that in the halogenobenzenes.



This is established by the opposing effect of solvents in these two series. The *p*-halogeno-diphenyls absorb at longer wavelengths in ethanol than in hexane. It is also supported by the fact that on introduction of the fluorine atom a blue shift results.

This shift is characteristic for all systems in which the fluorine atom is at the "receiving" end of the electronic migration, e.g. for *p*-fluoro aniline and *p*-fluorophenol.

This reversal of the solvent effect in the halogeno-substituted diphenyls as compared with the benzene derivatives is due to the electron shift in the ground state in the second C_6H_5- C group induced by the introduction of the halogen atom into the first phenyl group. This electron shift increases the polarizability of the system (C_6H_5—C_6H_4—Hal) towards the halogen atom and reduces it in the opposite direction i.e. a reversal of the relative polarizabilities of the overall absorbing system has occurred. The blue-shift due to the fluorine atom has been attributed to an appreciably smaller polarizability of the C-F electrons compared with those of the C—H bond.

The present investigation shows that, in agreement with these interpretations, the electronic migration in the *p*-halogeno-*p*-terphenyl series is in the same direction as that in the *p*-halogeno-diphenyls, i.e. towards the halogen atom. Again the fluorine is responsible for a blue shift and the K-band appears at longer wavelengths in the more polar ethanol than in hexane. As expected, the displacements are smaller than in the *p*-halogeno-diphenyls. However, the contribution of the polarity factor is indicated by the smaller decreases in ethanol as compared with that observed in hexane.

(d) *The effect of methyl and ammonium groups*

The effect of the methyl group is comparatively small, but as Burawoy and Spinner[9] have shown, the polarity factor is at least of the same degree as the polarizability of the C—CH_3 electrons. The former factor is responsible for the comparatively slight decrease of the red shift in the order of toluene > *p*-methyl-diphenyl > *p*-methyl-*p*-terphenyl.

The red shift due to the $\overset{+}{N}H_3$ group is greater in the *p*-terphenyl compound (31 Å) than in the diphenyl derivative (8 Å). Since it is known[6] that the polarizability of the C—$\overset{+}{N}H_3$ system is almost identical with that of the C—H bond, the observed displacement must be attributed to the increased polarity of the hydrocarbon system only. Thus, the third phenyl group in the *p*-terphenyl derivative, being more polar than in *p*-terphenyl itself, makes some contribution to the red-shift.

EXPERIMENTAL

The spectral determinations were carried out with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high tension spark being employed as the light source. All the investigated substances were obtained in a high state of purity. Most of the *p*-terphenyl compounds were prepared by the methods of France *et al.*,[10] *p*-cyano-, and *p*-fluoro-*p*-terphenyl have not been previously described.

p-*Fluoro*-p-*terphenyl*. *p*-Acetamino-*p'*-fluoro-diphenyl[11] (2 g) was dissolved in glacial acetic acid (100 cc) and acetic anhydride (20 cc) and phosphorus pentoxide (2·0 g) were added. The resultant solution was cooled to 10° and nitrous fumes (made from copper turnings and conc HNO_3) were passed into the cooled solution for 3 hr. The dark green solution was poured into water and the precipitated N-nitroso compound collected and dried under vacuum m.p. 85-86° (dec).

The dried unstable nitroso compound was allowed to react with dry benzene over a period of 3 days whence a brown tar formed and nitrogen was evolved. The tar was distilled under reduced pressure (10-3 mm) and *p*-fluoro-*p*-terphenyl (0·5 g) sublimed at 200°. The sublimate crystallizes from alcohol as colourless plates and needles of m.p. 214-215°. (Found: C, 86·8; H, 5·1. $C_{18}H_{13}F$ requires: C, 87·1; H, 5·2%).

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[10] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.* 1364 (1938).

[11] L. van Hove, *Chem. Zentr.* **1**, 312 (1923).

p-*Cyano*-p-*terphenyl*. *p*-Amino-*p*-terphenyl (0·5 g) was diazotized by the method of Pummerer and Bittner[12] and the diazo solution was added to a solution of potassium cuprocyanide (from 2 g copper sulphate). Nitrogen was evolved, and after 30 min the reaction mixture was heated to 50° on the steam bath. The precipitate formed was filtered off and extracted with ethanol and on cooling, *p*-cyano-*p*-terphenyl (0·1 g) crystallizes from alcohol as yellow platelets m.p. 219 220°. (Found: C, 89·1. H, 5·3; $C_{19}H_{13}N$ requires: C, 89·4; H, 5·1%).

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[12] R. Pummerer and K. Bittner, *Ber. Dtsch. Chem. Ges.* 57, 84 (1924).