Tetrahedron, 1960. Vol. 10. pp. 109 to 117. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRONIC SPECTRA OF ORGANIC MOLECULES AND THEIR INTERPRETATION—VII*

THE EFFECT OF TERMINAL NITRO AND AMINO GROUPS ON THE ELECTRONIC SPECTRA OF CONJUGATED HYDROCARBON SYSTEMS

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Abstract—The effect of terminal nitro and amino groups of absorbing conjugated systems on the corresponding K-bands and, in particular, its dependence on the length of the substituted hydrocarbon system is discussed. It is confirmed that the position of a K-band is almost exclusively determined by the charge migration in one direction along the conjugated system. The interaction between a *p*-amino and a *p*-nitro group in the ground state of the *p*-nitro *p*′-amino derivatives of diphenyl, stilbene, and similar compounds (transmitted through the conjugated hydrocarbon system) decreases with the length of the conjugated system.

INTRODUCTION

Previous investigations by Burawoy[1] *et al.* have shown that the "effective" electronic migration along an absorbing system, as indicated by the long arrow in I, determines the transition energy, i.e. the position of the corresponding K-band. The contribution of the accompanying "complementary" electron migration in the opposite direction is only small and can generally be neglected in qualitative comparative discussions.

$$\text{I. }\underrightarrow{\text{A -(CH}\quad\text{CH)}_n\text{– B}}$$

It has also been shown[1] 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) An electron shift (in the ground state) of the substituted system which will increase its electronic polarizability in the direction of the shift and facilitate the electronic migration.

(b) An increase of the electronic polarizability of the terminal group itself.

More recent experimental evidence[2] shows that the degree of stabilization of the excited state, i.e. the red shift of a K-band due to the perturbation not only by a terminal vinyl group, but also by any other substituent, decreases as the length of the substituted absorbing system increases.

This investigation deals, in greater detail, with the dependence of the effect of terminal nitro and amino groups (at both the electron receiving and electron donating end of the absorbing system) on the length of the substituted system. This involves the examination of a series of mono-*p*-nitro, mono-*p*-amino, *p*:*p*′-dinitro, *p*:*p*′-diamino, and *p*:*p*′-nitroamino-hydrocarbons such as benzene, diphenyl, terphenyl, quaterphenyl stilbene and tolane.

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* Part VI: *Tetrahedron* **10**, 102 (1960).

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[1] A. Burawoy, *Tetrahedron* **2**, 122 (1958); A. Burawoy and E. Spinner, *J. Chem. Soc.* 2035, 2557 (1955); A. Burawoy and A. R. Thompson, *J. Chem. Soc.* 4314 (1956).

[2] P. Brocklehurst, A. Burawoy and A. R. Thompson, *Tetrahedron* **10**, 102 (1960).

DISCUSSION

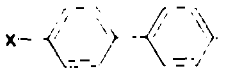
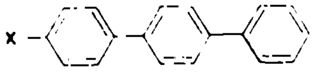
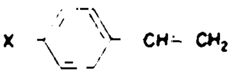
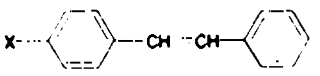
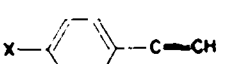
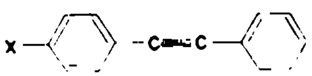
(a) *Spectra of* p-*nitro derivatives*

Data for the maxima and intensities of the K-bands of benzene, diphenyl, terphenyl, styrene, phenylacetylene, stilbene, tolane, and their *p*-mononitroderivatives in hexane and ethanol solutions are shown in Table 1, together with the displacements (D) due to the introduction of the nitro group.

The effective electronic migration of the transition corresponding to the K-band of the nitro derivatives is towards the nitro group as indicated by a long arrow in II.

It has already been shown[2] for the polyphenyl series that the introduction of the

TABLE 1. MAXIMA OF K-BANDS IN Å

Substance	Solvent	X — H		X — NO_2		D
		$\lambda_{max.}$ Å	$\epsilon_{max.}$	$\lambda_{max.}$ Å	$\epsilon_{max.}$	
	Ethanol	2030	—	2595	9500	565
	Hexane	2020	6600	2513	9000	493
	Ethanol	2475[a]	19,500	3060[a]	18,000	585
	Hexane	2467[a]	19,000	2935[a]	18,000	468
	Ethanol	2769[a]	32,000	3260[a]	21,000	491
	Hexane	2750[a]	32,000	3150[a]	26,000	400
	Ethanol	2453[a]	15,000	3010[a]	14,500	557
	Hexane	2450[a]	14,000	2895[a]	15,500	445
	Ethanol	2935	20,000	3400	17,500	465
	Hexane	2920	19,500	3325	19,500	405
	Ethanol	2346[a] 2444 2395[c]	15,000 13,500	2860[a]	15,000	465
	Hexane	2351[a] 2446 2398[c]	15,500 13,500	2798[a]	16,000	400
	Ethanol	2775 2960 2860[c]	33,000 29,000	3230	23,000	370
	Hexane	2775 2960 2860[c]	34,000 29,000	3200	25,000	340

C = centre of band system.

[a] A. Burawoy and J. P. Critchley, *Tetrahedron* 5, 340 (1959).

nitro group into benzene and diphenyl, to give nitrobenzene and *p*-nitrodiphenyl respectively, has similar effects on their spectra, because in the latter case the expected smaller displacement due to the decreasing contribution of the electronic polarizability

$$\text{II. } \underset{\longrightarrow}{\text{Ar-NO}_2}$$

of the C-NO$_2$ group is enhanced by the contribution of the electron-shift in the ground state of the second phenyl group in *p*-nitrodiphenyl.

In *p*-nitroterphenyl, however, the polar effect is transmitted to the third phenyl group to a much lesser degree. The bathochromic displacement due to the resultant electron-shift is now unable to make up for the reduced displacement caused by the decreasing contribution of the polarizability of the C–NO$_2$ system. Thus, the displacement observed is only 491 Å in ethanol, 400 Å in hexane compared with that in nitrobenzene (D = 565; 493 Å) and *p*-nitrodiphenyl (D = 585; 468 Å).

The effect of the nitro group in *p*-nitrostyrene (D = 557; 445 Å) is again similar to that observed for *p*-nitrodiphenyl (D = 585; 468 Å), but is somewhat smaller in *p*-nitrophenylacetylene (D = 465; 400 Å). Burawoy and Critchley[3] have shown that electron-shifts in triple bonds are responsible for smaller increases in the polarizabilities of these bonds than similar shifts in double bonds, and they attributed the reduced bathochromic effect of the nitro group (in *p*-nitrophenylacetylene) partly to this factor.

In *p*-nitrostyrene, the electron-shift caused by the nitro group results in an increase of the polarizability of the C–CH=CH$_2$ electron system towards the benzene ring and confers a slightly electron-repelling character to the vinyl group, whereas in *p*-nitrophenylacetylene the electron-attracting character of the —C≡CH group is preserved. Thus, the electron-attracting acetylene group is responsible for an electron-shift in the nitro group in opposition to the effective charge migration, i.e. a reduction in the polarity of the C–NO$_2$ group and consequently a reduction in its polarizability towards the oxygen atoms. This is an additional factor responsible for the reduced bathochromic effect of the nitro group in *p*-nitrophenylacetylene.

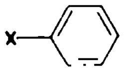
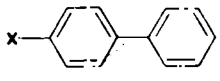
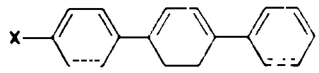
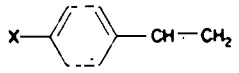
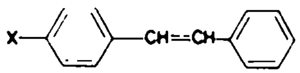
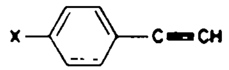
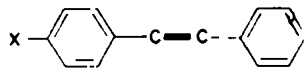
The bathochromic effect of the nitro group observed for *p*-nitrostilbene (D = 465; 405 Å) and *p*-nitrotolane (D = 370; 340 Å) in ethanol and hexane solutions is much less than the effect of the nitro group observed in the case of *p*-nitrostyrene (D = 557; 445 Å) and *p*-nitrophenylacetylene (D = 465; 400 Å) respectively. These observations are analogous to those made for *p*-nitroterphenyl. Again the polar effect caused by the introduction of the nitro group is transmitted to the additional phenyl group to a smaller degree.

(b) *Spectra of* p-*amino derivatives*

Data for the maxima and intensities of the K-bands of the investigated hydrocarbons and their *p*-monoamino derivatives in hexane and ethanol solution, together with the displacements (D) due to the introduction of the amino group are shown in Table 2.

In the case of *p*-aminophenylacetylene, the electron-attracting acetylene group causes an electron-shift in the H$_2$N–C group which coincides with the direction of the effective charge migration. This is in contrast to *p*-nitro-phenylacetylene where the electron-attracting acetylene group causes an electronic-shift in the nitro group in opposition to the effective charge migration. Thus, the effect of the nitro group in *p*-nitro-phenylacetylene is considerably smaller than in *p*-nitro-styrene, whereas the acetylene bathochromic displacement due to the introduction of the amino group is only slightly less for *p*-aminophenylacetylene than for *p*-aminostyrene.

TABLE 2. MAXIMA OF K-BANDS IN Å

Substance	Solvent	X—H		X—NH$_2$		D
		$\lambda_{max.}$ Å	$\Sigma_{max.}$	$\lambda_{max.}$Å	$\Sigma_{max.}$	
	Ethanol	2030	–	2344	8000	314
	Hexane	2020	6600	2340	7500	320
	Ethanol	2475^{a}	19,500	2805^{a}	19,000	330
	Hexane	2467^{a}	19,000	2744^{a}	19,000	277
	Ethanol	2769^{a}	32,000	3010^{a}	32,000	241
	Hexane	2750^{a}	32,000	2959^{a}	27,000	209
	Ethanol	2453^{a}	15,000	2770^{a}	16,000	317
	Hexane	2450^{a}	14,000	2728^{a}	19,000	278
	Ethanol	2935	20,000	3180	18,500	245
	Hexane	2920	19,500	3150	24,000	230
	Ethanol	2346^{a} 2444 $\overline{3295}^{C}$	15,000 13,500	2697^{a}	20,500	302
	Hexane	2351^{a} 2446 $\overline{2398}^{C}$	15,500 13,500	2650^{a}	20,500	252
	Ethanol	2775 2960 $\overline{2860}^{C}$	33,000 29,000	3100	28,000	150
	Hexane	2775 2960 $\overline{2860}^{C}$	14,000 29,000	3010	28,000	150

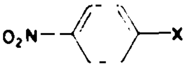
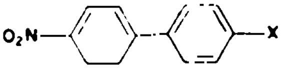
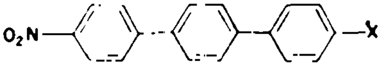
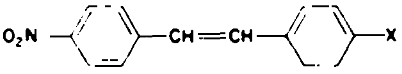
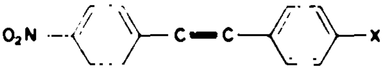
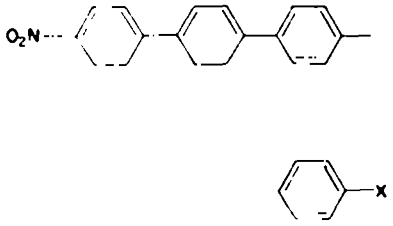
C centre of band system.

Similar differences are observed for the corresponding stilbene and tolane derivatives.

(c) *Spectra of* p:p′*-dinitro and* p:p′*-diamino derivatives*

Data for the maxima and intensities of the K-bands of the *p*:*p*′-dinitro and *p*:*p*′-diamino derivatives of benzene, diphenyl, terphenyl, stilbene and tolane in ethanol solution, and the displacements on the introduction of the first (D) and of the second

TABLE 3

Substance	Solvent	X = H		X = NO$_2$		D	D′
		$\lambda_{max.}$ Å	$\varepsilon_{max.}$	$\lambda_{max.}$ Å	$\varepsilon_{max.}$		
	Ethanol	2595	9500	2061	13,000	565	+6
	Ethanol	3060[8]	18,000	3052	29,000	585	8
	Ethanol	3260	21,000	3310	73,000	491	+50
	Ethanol	3400	17,500	3415	18,500	465	+15
	Ethanol	3230	23,000	3270	31,000	370	+40
	Dimethyl-formamide	—	—	3550	40,000	—	—

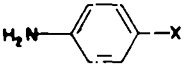
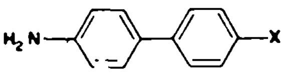
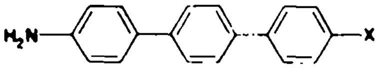
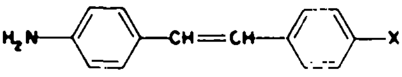
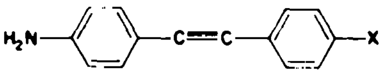
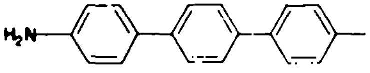
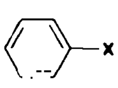
substituents (D′) are summarized in Tables 3 and 4. Many of the disubstituted derivatives were insoluble in hexane and therefore could not be investigated in this solvent (those of quaterphenyl are investigated in dimethyl formamide).

In the case of the nitro derivatives, the second electron attracting nitro group is at the electron-donating end of the effective charge migration, the direction of which is indicated by the long arrow in III.

$$\text{III. } \underset{\xrightarrow{\hspace{10em}}}{O_2N\text{—}(CH{=}CH)_n\text{—}NO_2}$$

It is responsible for an electron-shift in the opposite direction to the effective charge

TABLE 4. MAXIMA OF K-BANDS IN Å

Substance	Solvent	X = H		X = NH$_2$		D	D′
		$\lambda_{max.}$ Å	$\Sigma_{max.}$	$\lambda_{max.}$ Å	$\Sigma_{max.}$		
	Ethanol	2344	8000	2440	11,000	314	+96
	Ethanol	2805[a]	19,000	2845	28,000	330	+40
	Ethanol	3010	32,000	3127	40,000	241	+117
	Ethanol	3180	18,500	3290	27,000	245	+110
	Ethanol	3100	28,000	3120	34,000	240	+20
							
	Dimethyl-formamide	—	—	3400	58,000	—	—

migration and, therefore, could be expected to cause a blue-shift of the K-band. This effect is balanced by the electronic polarizability of the C–NO$_2$ system towards the carbon atom, which should be considerably smaller than in the opposite direction. Thus negligible band displacements, to shorter or longer wavelengths, are observed on the introduction of the second nitro group.

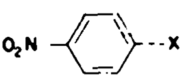
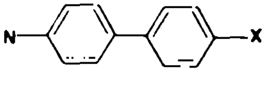
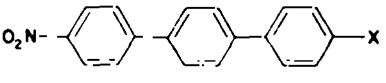
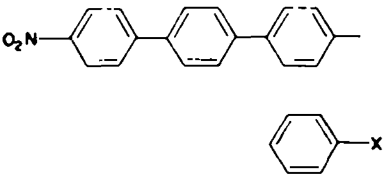
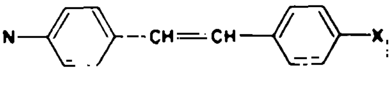
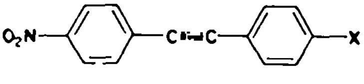
Similarly, the second electron-repelling amino group in the *p*:*p*′-diamino derivatives is responsible for an electron-shift in the opposite direction to the effective charge migration of the transition. This should cause a slight hypsochromic band displacement. However, the blue shift is masked by the effect of the polarizability of the

C–NH_2 electron system towards the amino group which is, again, smaller than in the opposite direction. This results in moderate displacements of the K-bands to longer wavelengths (20–117 Å) which may be compared with the much greater effect of the first amino group (240–314 Å).

(d) *Spectra of* p:p′*-nitroamino compounds*

The maxima and intensities of the K-bands of the *p*-nitro- and the *p*:*p*′-nitroamino derivatives of benzene, diphenyl, terphenyl, stilbene and tolane in ethanol solution and, as far as solubility allows, in hexane solution are shown in Table 5. (*p*:*p*′-Nitroaminoquaterphenyl is determined in dimethyl formamide.) The displacements (D) due to the introduction of the amino group into the nitrobenzene derivatives, the displacements (D′) observed on the introduction on the amino group into the corresponding hydrocarbons and the difference between these displacements (D*) are also shown.

TABLE 5. MAXIMA OF BANDS OF *p*:*p*′-NITROAMINO DERIVATIVES (Å)

Substance	Solvent	X = H		X = NH_2		D	D′	D*
		λ_{max} Å	Σ_{max}	λ_{max} Å	Σ_{max}			
	Ethanol	2595	9500	3725	16,800	1130	314	816
	Ethanol	3060[3]	18,000	3775	13,800	715	330	385
	Ethanol	3200	21,000	3580	16,500	380	241	139
	Dimethyl-formamide	—	—	3400	37,000	—	—	—
	Ethanol Hexane	3400 3325	17,500 19,500	4090 3800	23,000 17,000	690 475	245 230	445 245
	Ethanol Hexane	3230 3200	23,000 25,000	3890 3640	18,500 19,500	660 440	240 150	420 290

The latter values (D*) give an approximate measure of the enhanced polarity resulting from the interaction of the terminal nitro and amino groups of the conjugated system.

It can be seen that the polarities of the systems will be much greater than those in the corresponding *p*-mononitro- and *p*-monoamino-derivatives respectively. The reinforced electron-shifts within the *p*:*p*′-nitroamino compounds coincide with the direction of the effective charge migration of the transition as indicated by the long arrow IV.

$$\text{IV.}\quad \underleftarrow{\mathrm{O_2N{-}(CH\quad CH)_n{-}NH_2}}$$

They are responsible for increased electron polarizabilities and therefore large bathochromic displacements of the K-bands.

It is interesting to note that D^* decreases in the order *p*-nitroaniline (816 Å) > *p*:*p*′-nitroaminodiphenyl (385 Å) > *p*:*p*′-nitroaminoterphenyl (139 Å). This clearly indicates that the interaction of the nitro and amino groups transmitted through the hydrocarbon system falls off rapidly with the increased length of the conjugated polyphenyl system.

Even more significant is the fact that the K-band, appearing at 3725 Å for *p*-nitroaniline, is only slightly displaced to 3775 Å for *p*:*p*′-nitroaminodiphenyl, and, in spite of the increased length of the conjugated system, undergoes blue-shifts for *p*:*p*′-nitroaminoterphenyl (3580 Å) and for *p*:*p*′-nitroaminoquaterphenyl (3400 Å). The bathochromic shift expected from the introduction of each additional phenyl group is cancelled in the terphenyl and quaterphenyl derivatives by the effect due to the decreasing interaction of the terminal amino and nitro groups.

In the case of the stilbene and tolane derivatives, the interaction of these groups is of the same order as observed for *p*:*p*′-nitroaminodiphenyl, in spite of the introduction of the additional vinyl and acetylene groups. This clearly indicates that the transmission of polar effects through aliphatic unsaturated groups is considerably greater than that through a phenyl group. It also shows that the transmission is of the same order for both double and triple bonds groups.

EXPERIMENTAL

The spectra were determined with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light.

All the compounds were obtained in a high state of purity.

p-*Nitro*-p′-*amino-tolane*. Sodium hydrosulphide solution (prepared by dissolving sodium sulphide (2·4 g) in water (30 cc) and saturating with hydrogen sulphide) was added slowly with stirring to a suspension of finely powdered dinitrotolane[4] (3 g) in boiling ethanol (75 cc). The solution was refluxed for a further ½ hr and then allowed to cool. The reddish brown precipitate was filtered, and dried over calcium chloride in a vacuum desiccator. Crystallization from nitrobenzene afforded shining red plates of m.p. 210–211°. Yield: 1·6 g (61%). (Found: C, 69·7; H, 4·4; N, 11·9. $C_{14}H_{10}O_2N_2$ requires: C, 70·6; H, 4·2; N, 11·8%).

p-*Nitrotolane*. A solution of potassium hydroxide (0·65 g 2·5 moles KOH per mole dichloride) in ethanol (6 cc) and water (1 cc) was added dropwise during 10 min, with stirring, to a boiling solution of *p*-nitrostilbene dichloride[5] (1·3 g) in ethanol (20 cc). The solution was refluxed for a further ½ hr, cooled, and filtered to remove potassium chloride. Water (100 cc) was added to the mother liquor, and the solution was extracted with ether. The combined fractions were dried over anhydrous sodium sulphate. Removal of the solvent gave a yellowish-white solid (0·2 g 21%).

Crystallization from light petroleum (b.p. 60–80°) gave pale yellow microflakes of m.p. 121–122°. (Found: C, 75·3; H, 4·0; N, 6·5. $C_{14}H_9NO_2$ requires: C, 75·4; H, 4·0; N, 6·3%).

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p-*Aminotolane.* Zinc dust (1 g) was added in small portions to a solution of *p*-nitrotolane (0·1 g) in ethanol (16 cc) with good stirring. Conc. HCl (4 g) was added dropwise, the temp. being maintained between 15–20° throughout the addition. Stirring was continued for 2·5 hr, and the solution filtered. Dil. H_2SO_4 (25%, 5 cc) was added to the filtrate and a white precipitate of *p*-aminotolane sulphate separated. Basification with sodium hydroxide solution afforded a white precipitate. Crystallization from aqueous ethanol gave white needles m.p. 127 128°. (Yield: 0·05 g 58%). (Found: C, 87·4; H, 5·6; N, 7·1. $C_{14}H_{11}N$ requires: C, 87·0; H, 5·7; N, 7·3%).

p-*Nitro*-p′-*aminoterphenyl.* *p*:*p*′-Dinitroterphenyl[6] (8 g) was dissolved in pyridine (200 cc) and a solution of crystalline sodium hydrosulphide [made by saturating a solution of crystalline sodium sulphide (5·3 g) in water (20 cc) with hydrogen sulphide] was added during 15 min at the boil. The reaction mixture was refluxed for a further 15 min. Removal of the pyridine by distillation, the last portion under reduced pressure, afforded an orange-brown solid. (Yield: 6·5 g 92·7%). Crystallization from nitrobenzene gave golden plates m.p. 304°. (Found: C, 73·9; H, 4·8; N, 9·5. $C_{18}H_{14}N_2O_2$ requires: C, 74·4; H, 4·8; N, 9·6%).

p:p′-*Diaminoterphenyl.* A solution of sodium hydrosulphide [made by saturating a solution of crystalline sodium sulphide (5·5 g) in water (20 cc) with hydrogen sulphide] was added to a boiling solution of *p*:*p*′-dinitro-terphenyl[6] (4 g) in pyridine (200 cc) and the mixture was refluxed for 2 hr. Removal of the pyridine by distillation, the last portion under reduced pressure, afforded a yellow solid. Crystallization from ethanol gave yellow plates of m.p. 242–243°. (Yield: 2·4 g 80%). (Found: C, 83·3; H, 6·3. $C_{18}H_{16}N_2$ requires: C, 83·1; H, 6·4%).

p-*Nitro*-p′-*amino-quaterphenyl.* A solution of crystalline sodium sulphide (1·1 g) in water (20 cc) was saturated with hydrogen sulphide and pyridine (20 cc) added to the solution. *p*:*p*′-Dinitroquaterphenyl[7] (2 g) was dissolved in pyridine (200 cc) and heated to the boil. The hydrosulphide was added over ½ hr and the mixture was allowed to boil for a further ½ hr. Excess pyridine was then distilled off, the final traces being removed under reduced pressure. The product so obtained was crystallized from dimethylformamide as red-brown plates of m.p. 345° dec. (Yield: 1·1 g 61%). (Found: C, 81·0; H, 5·2; N, 7·6. $C_{24}H_{18}N_2O_2$ requires: C, 80·9; H, 5·1; N, 7·8%).

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