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ON THE SPECTRA OF SOME ACCEPTOR-TYPE POLYNITRO DERIVATIVES OF BIPHENYL, BIPHENYLMETHANE AND BIPHENYLAMINE

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The UV and visible spectra of nitro and polynitro derivatives of biphenylamine were investigated and the substituent effects were interpreted in comparison with the corresponding biphenyl and biphenylmethane derivatives.

Introduction

It is well known [1-5] that polynitro aromatic compounds act as acceptor molecules and form stable molecular complexes with, for example, aromatic Schiff bases [6-8]. It has been stated that if any nitro group is prevented from assuming a coplanar arrangement with the attached ring, then the polynitro compound will be a less effective complexing agent. For example, trinitrobenzene forms more stable complexes with aromatic hydrocarbons than either trinitrotoluene or picric acid does. Both polar and steric factors may be responsible for this decrease in the complexing ability [9].

We have prepared a series of molecular complexes of aromatic Schiff bases as donors with different polynitro compounds as acceptors and studied their UV and visible spectra. The spectra of aromatic Schiff bases have already been discussed in several papers [e.g. 10-12]; in this work, a short review is primarily given of the spectral behaviour of the polynitro acceptor molecules.

Experimental

The compounds investigated were Merck p.a. chemicals. The UV and visible spectra were determined on a SPECORD UV-VIS spectrophotometer, in quartz cells. The solvents were commercially available, spectroscopically pure solvents. The acidic and basis solutions contained 0.1 mol/dm^3 H_2SO_4 or NaOH in methanol.

The twist angles θ_N were calculated by using the formula $\cos^2 \theta_N = \varepsilon / \varepsilon_0$, where ε and ε_0 are the molar extinctions of the compound investigated and the planar (quasi-planar) form, respectively.

Results and Discussion

Before a discussion of the spectral behaviour of biphenylamines, it is interesting to compare the corresponding nitro derivatives of biphenyl (BP), biphenylmethane (BPM) and biphenylamine (BPA). Some data are presented in Table I.

The spectrum of BP shows an intense band at 252 nm, which corresponds to the ^1L_a benzene band; the forbidden lower-in-

Table I

λ_{max} *and* *log*ε *values of* BP, BPM, BPA *and their substituted derivatives*

Positions of nitro groups		λ/nm(logε)				
		BP		BPM		BPA
none	a	252(4.26)13)	c	268(2.61)16)	d	285(4.31)
2	b	296(3.30)14)	c	254(3.66)17)	d	425(3.87)
4	b	295(4.20)14)	c	278(4.02)17)	d	392(4.34)
2,2′	b	253(4.10)15)	c	256(4.00)18)	d	420(3.97)19)
4,4′	b	295(4.00)15)	c	277(4.36)	d	404(4.57)
2,4	b	265(4.02)15)	d	262(4.12)	c	350(4.23)

a: cyclohexanone; b: isooctane+ 2% CH_2Cl_2; c: ethanol;
d: methanol

tensity ^1L_b band is hidden below this band [20].

Pauling [9] suggested that steric interactions between the *ortho* hydrogens should result in a non-coplanar conformation; the interplanar angle in the solution state is about 20° [21]. Theoretically, *cis* and *trans* conformations are possible for 2,2′ derivatives, but electron diffraction data [22, 23] indicate that the 2,2′-dihalogeno-BP derivatives, for example, have a *cis* configuration. The effect of 2,2′ substituents is very important. For instance, 2,2′, 6,6′-tetrachloro-BP is known to be a true biradical [24]. In 4-amino-4′-nitro-BP, the 4′-nitro group exerts a marked effect on the basicity of the 4-NH_2 group, but this effect is diminished by 2 or 2,2′ substituents because these groups block the nitro-amine resonance through the forced non-coplanarity of the conformation of the BP skeleton [25].

Due to the steric interference, the 2,2' derivative of BP departs from the coplanar conformation and the resonance is destroyed; the absorption is approximately that of two nitrobenzene molecules. 4,4-Dinitro-BP displays and increased intensity and the band is shifted to longer wavelengths, which can be attributed to the increased polarity of the excited state and to the lowering of the energy required to produce this state [26]. The data in Table I show that for the 2-nitro derivative the band is shifted towards longer wavelengths and the intensity decreases. Similar intensity decreases can be observed for the 2,2′ and 2,4 derivatives. The steric inhibition by the bulky nitro groups is obvious, and these compounds have a twisted conformation around the short (1.48 nm [9, 21]) central 1-1′ bond. The calculated twist angles θ_N for these three derivatives are 71, 36 and 41°, respectively.

Toluene shows the ^1L_a benzene band at 261 nm ($\log\varepsilon$= 2.35) [14], while BPM has a band at 268 nm ($\log\varepsilon$=2.61) [16]; i.e. the two phenyl rings behave as two separate chromophores. However, a comparison of the spectra of 4-nitrotoluene and 4,4′-dinitro-BPA reveals that this relationship is not valid. Derivatives containing NO_2 groups in the 2 or 2,2′ positions also exhibit a decreased intensity compared to that for the 4 or 4,4′ derivatives.

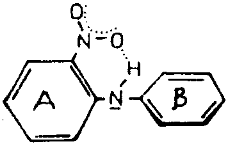
The spectrum of aniline contains two bands at 235 (3.98) and 285 (3.22) nm, which correspond to the ^1L_a and ^1L_b bands of benzene, respectively. For the nitro derivatives, the ^1L_a band does not change considerably (223-239 nm), but the longer-wavelength band does. Due to nitro substitution in the *ortho* position in aniline, the $-NH_2$ group is twisted out of the plane of the ring, and the nitrogen bond angles become more pyramidal; consequently, the promotion energy is lowered. For 4-nitroaniline, no steric interference occurs; calculation of the twist angles θ_N from the measured ε_{max} values for 2-, 2,4-, 2,6- and

2,4,6-nitroaniline gives 56°, 32°, 49° and 50°, respectively.

Introduction of a second benzene ring into the aniline system results in a considerable intensity increase, and the new ring may be assumed to be perpendicular or nearly perpendicular to the plane of the C-N bond and the unshared pair [27]. The spectral data on a series of nitro derivatives of BPA are presented in Table II; our data are in accordance with the literature data [e.g.. 28-30]. Since the basic and acidic characters of donors and acceptors, respectively, are very important from the aspect of the formation of molecular complexes, Table II also contains the pK_a values of several BPA derivatives.

2,2'-Alkyl substitution generally causes strong hypsochromic shifts, i.e. the steric hindrance and the non-coplanar conformation will raise the potential energy of the excited state, and hence the transition energy will be increased [31].

2-, 2,2'-, 2,6- and 2,2', 6,6'-nitro substitution causes a strong bathochromic shift (~420 nm) and the intensities decrease (Table II). In these cases, due to the steric interference of the nitro groups, ring *B* is not coplanar with the unshared electron pair of the central nitrogen atom, and the molecule has a twisted conformation (Structure I).



I

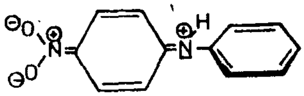
In the absence of an *ortho* substituent, e.g. in 4-nitro-BPA, the increased conjugation (which may be crudely represented by resonance form II) tends to change the bonding around the nitrogen atom from a tetrahedral towards a trigo-

Table II

UV and visible spectral data on NO_2 substituted biphenylamines

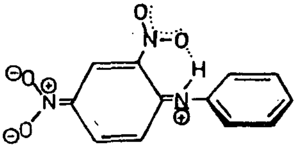
Positions of nitro groups	Solvent	λ/nm (logε)			θ_N	pK_a^*
none	MeOH	208(4.33)		285(4.31)		
2	MeOH	220(4.12)	257(4.16)	425(3.87)	53°	17.57
2,2',6,6'	MeOH	229(4.18)		418(3.87)	53°	
2,2'	MeOH	225(4.18)	264(4.22)	420(3.97)[19]	47°	
2,6	MeOH	228(4.18)	256(4.44)	424(3.90)	39°	
2,2',4,4',6,6'	MeOH	208(4.16)		385(4.09)	39°	2.63
2,4,6	EtOH	233(4.29)		367(4.12)	37°	10.38
2,4'	EtOH	245(4.23)	351(4.08)	405(4.14)[19]	35°	13.84
2,2',4	EtOH	228(4.26)	253(4.19)	372(4.16)[19]	33°	
2,2',4,6	MeOH	225(4.21)		374(4.18)	31°	
2,4	EtOH	231(4.11)		350(4.23)	24°	
2,2',4,6,6'	EtOH	234(4.22)		379(4.24)	23°	
2,4,4',6	MeOH	231(4.29)		381(4.29)	12°	8.88
4	MeOH	226(3.80)	257(4.05)	392(4.34)		15.90
4,4'	MeOH	233(4.10)		404(4.57)		14.08
2,4,4'	EtOH	224(4.24)		366(4.33)[19]		12.35
2,2',4,4'	EtOH	219(4.35)	358(4.24)	401(4.36)[19]		10.82
2,2',4,4',6	MeOH	221(4.31)	351(4.25)	409(4.41)		6.72

* Stewart, R., J.P. O'Donnell: J. Amer. Chem. Soc., <u>84</u>, 493 (1962)



II

nal configuration [27]. This decreases the C-N bond length because of the increased double bond character of the bond, and hence it is more susceptible to steric effects. In contrast, the bands of BPA derivatives containing nitro groups in the 4 or 4,4' positions are shifted hypsochromically, the intensities are slightly decreased and the calculated twist angles are also lower. A similar effect may be observed for the 2,4-dinitro derivative (Structure III).



III

The situation more complicated is for this group of compounds relative to the BP and BPM derivatives. In this case the non-bonding electron pair of the central nitrogen atom also participates in the formation of a quinoidal system, which causes a strong bathochromic shift of the bands. The intensity decrease is related to the value $\cos^2\theta$ for the twist angle θ_N [e.g. 14, 32-34]. If we assume that the 285 nm band of BPA corresponds to the band at around 350-420 nm of the nitro derivatives and that BPA is nearly planar, the twist angles can be calculated; the values are presented in Table II. It may be stated that the introduction of the first nitro group into the 2 position causes the greatest twisting; further substitution in the 2' or/and 6,6' positions results in no more change in the conformation, whereas nitro groups in the 4 or 4,4' positions decrease the twist angle.

In the case of BP derivatives, the steric inhibition of the nitro group(s) is the determinant effect, while for the BPA derivatives the conjugation of the nitro group(s) together with the nitrogen lone pair also plays an important role.

Table III lists the maximum data for the long-wavelength band of 2,2', 4,4',6,6'-hexanitro-BPA (dipicrylamine), measured in different solvents. The solvents can be divided into three groups. In benzene, 1,4-dioxane, chloroform and dichloromethane, the 385 nm band of dipicrylamine does not vary considerably. The intensity is markedly high in chloroform solution, probably due to the intermolecular interaction between the chloroform and the nitro groups [27]. In alcohols, the band shifts in the sequence MeOH < EtOH < n-PrOH < i-PrOH and the intensities alter, too. This sequence is the same as that of the relative permittivities of the alcohols.

Table III

UV and visible spectral data on dipicrylamine in different solvents

Solvent	λ/nm (logε)	Solvent	λ/nm (logε)
Dioxane	378(4.12)	EtOH	406(3.93)
Benzene	383(4.24)	MeOH	385(4.09)
$CHCl_3$	383(4.40)	CH_3CN	423(4.51)
CH_2Cl_2	382(4.27)	DMSO	430(4.72)
i-PrOH	418(4.54)	MeOH/Acid	378(4.10)
n-PrOH	417(4.43)	MeOH/Base	420(4.43)

It seems that the polarization effect of the solvent molecules plays an important role, but the active hydrogen atom of the alcohols must also be taken into account. Higher bathochromic shifts are observed in DMF and DMSO solutions, which may be interpreted via the high polarization effects of these solvents, as a result of which an increased conjugated system is formed. A similar situation can be observed in strong basic solution, in which dipicrylamine is present almost entirely as an anion [35], while in acidic medium the spectrum does not change significantly.

References

[1] *Briegleb, G., J. Czekalla*: Angew. Chem. *72*, 401 (1960).

[2] *Briegleb, G., H. Delle*: Z. Elektrochem., *64*, 347 (1960).

[3] *Briegleb, G., J. Czekalla*: Z. physik. Chem., N.F. *24*, 37 (1960).

[4] *Foster, R., T.J. Thomson*: Trans. Farad. Soc., *59*, 2287 (1961).

[5] *Foster, R., C.A. Fyfe*: Trans. Farad. Soc., *61*, 1626 (1965).

[6] *Issa, R.M., M. Graber, A.L. El-Ansary, H.F. Rizk*: Bull Soc. Chim. France, 173 (1985).

[7] *Hindawey, A.M., Y.M. Issa, R.M. Issa, H.F. Rizk*: Acta Chim. Hung.,Budapest, *112*, 415 (1983).

[8] *Issa, Y.M.*: Spectrochim. Acta, *40A*, 137 (1984).

[9] *Pauling, L.*: The Nature of the chemical Bond, 2nd ed., Cornell Univ. Press, Ithaca, 1942., p. 220
Newman, M.S.: Steric Effects in Organic Chemistry., J. Wiley and Sons, N.Y. 1956. p. 473.

[10] *Császár, J.*: Acta Phys. Chem., Szeged, *25*, 137 (1979).

[11] *Császár, J., J. Balog, A. Makáry*: Acta Phys. Chem., Szeged, *24*, 473 (1978) and references cited therein

[12] *Brocklehurst, P.*: Tetrahedron, *18*, 299 (1961)

[13] *Friedel, R.A., M. Orchin*: Ultraviolet Spectra of Aromatic Compounds., J. Wiley and Sons, N.Y. 1951.

[14] *DeTar, D.F., H.H. Scheifele*: J. Amer. Chem. Soc., *73*, 1442 (1951).

[15] *DeTar, D.F., A.A. Kazini*: J. Amer. Chem. Soc., *77*, 3842 (1955).

[16] *Habert, R., J. Derkoch*: Monatsh. Chem., *88*, 47 (1957).

[17] *Dewar, M.J.S., D.S. Orel*: J. Chem. Soc., 3079 (1958).

[18] *Margerum, J.D., L.J. Miller, E. Saito, M.S. Brown, H.S. Mosher, R. Hardwick*: J. Phys. Chem. *66*, 2434 (1962).

[19] *Schroeder W.A., P.E. Wilcox, K.N. Trueblood, A.O. Dekker*: Anal. Chem., *23*, 1740 (1951).

[20] *Jaffé, H.H., M Orchin*: Theory and Application of Ultraviolet Spectroscopy., J. Wiley and Sons, N.Y. 1964. p. 408.

[21] *Suzuki, H.*: Bull. Chem. Soc. Japan, *32*, 1340 (1959).

[22] *Bastiansen, O.*: Acta Chem. Scand., *3*, 408 (1949).

[23] *Bastiansen, O., L. Snodvik*: Acta Chem. Scand., *8*, 1593 (1954).

[24] *Müller, E.*: Chem. Ber., *72*, 2063 (1939).

[25] *Sherwood, D.W., M. Calvin*: J. Amer. Chem. Soc., *64*, 1350 (1942).

[26] *Radebush, W.H.*: Chem. Rev., *41*, 317 (1947).

[27] *Balasubramanian, A., J.B. Capindale, W.F. Forbes*: Canad. J. Chem., *42*, 2674 (1964).

[28] *Stewart, R.S., J.P. O'Donnell*: Canad. J. Chem., *42*, 1681 (1964).

[29] *Bell, M.G.W., M. Day, A.T. Peters*: J. Chem. Soc., 132 (1967).

[30] *Balaban, A.T., P.T. Frangopol, M. Frangopol, N. Negoită*: Tetrahedron, *23*, 4661 (1967).

[31] *Remington, W.R.*: J. Amer. Chem. Soc., *67*, 1838 (1945).

[32] *Beale, R.N., E.M.F. Roe*: J. Amer. Chem. Soc., *74*, 2302 (1952).

[33] *Hawthorne, F., D.J. Cram*: J. Amer. Chem. Soc., *74*, 5859 (1952).

[34] *Braude, E.A., F. Sondheimer*: J. Chem. Soc., 3754 (1955).

[35] *G. Schill*: Anal. Chim. Acta, *21*, 341 (1959).

О СПЕКТРАХ НЕКОТОРЫХ ПОЛИНИТРО ПРОИЗВОДНЫХ АКЦЕПТОРНОГО ТИПА БИФЕНИЛА, БИФЕНИЛМЕТАНА И БИФЕНИЛАНИЛИНА

Й. Часар

Изучены спектры интро- и полинитро производных бифениланилина в ультрафиолетовой и видимой областях и рассмотрено влияние заместителей при сравнении с соответствующими бифенил и бифенилметановыми производными.