THE ELECTRONIC SPECTRA OF THE NITRONAPHTHYLAMINES

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Abstract—The ultra-violet absorption spectra of all fourteen nitronaphthylamines have been measured in polar and non-polar solvents. The first absorption band undergoes a bathochromic shift on changing from a non-polar to a polar solvent. An attempt has been made to correlate the magnitude of this bathochromic shift with mesomeric interaction and intramolecular hydrogen bonding in the nitronaphthylamines.

INTRODUCTION

THE ultra-violet absorption spectra of pure specimens of the nitronaphthylamines have been measured, using a photoelectric spectrophotometer, in cyclohexane and ethanol solutions. This is the first occasion that the spectra of all fourteen nitronaphthylamine isomers have been reported and previous studies[1-3] of these compounds have used the photographic recording method.

The first absorption band of the nitronaphthylamines, which is due to mesomeric interaction between the nitro and amino groups, undergoes a large bathochromic shift on changing from a non-polar to a polar solvent. In the ground state, in a non-polar solvent, a nitronaphthylamine molecule can be represented by state I. On changing to a hydrogen bonding, polar solvent, such as ethanol, the same nitronaphthylamine molecule may be represented by state Ia, due to the development of partial charges by mesomeric interaction. When light is absorbed the molecule is raised to the first excited state II; this change is observed as the first absorption band.
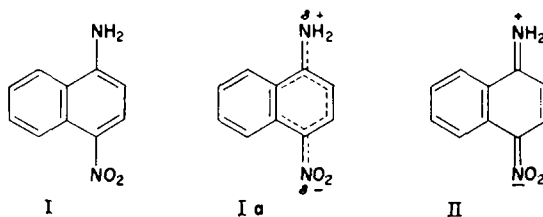
The energy difference between states Ia and II is less than that between states I and II. Hence less energy is required to excite a nitronaphthylamine molecule in a polar than in a non-polar solvent thus explaining the observed bathochromic shift. In nitronaphthylamine molecules where intramolecular hydrogen bonding occurs, between an oxygen atom of the nitro group and a hydrogen atom of the amino group, solvation is reduced leading to a smaller bathochromic shift.

Mesomeric interaction in the nitronaphthylamines results from the conjugation of

[1] L. Hertel-Danzig, *Z. Electrochem.* **47**, 813 (1941).
[2] H. H. Hodgson and H. S. Turner, *J. Soc. Dyers and Colourists* **59**, 218 (1943).
[3] H. H. Hodgson and D. E. Hathway, *Trans. Faraday Soc.* **41**, 115 (1945).

the lone pair of electrons on the amine nitrogen atom, through the π-electron system of the naphthalene nucleus with the p-electron system of the nitro group. The energy difference between a hypothetical nitronaphthylamine in which mesomeric interaction does not occur, possibly almost true for the 7- and 3-nitro-2-naphthylamines, and a nitronaphthylamine in which it does occur can be termed the energy of mesomeric interaction. The energy of mesomeric interaction would thus be determined by the distribution of π-electrons in the naphthalene nucleus and the conjugating powers of the carbon atoms to which the nitro and amino groups are attached.

Remington[4] and also Wepster[5] have used the intensity of the first absorption band of substituted nitranilines as a measure of mesomeric interaction and hence steric distortion of the substituent groups. Wepster[5] has used the criterion that the energy of mesomeric interaction in a *p*-nitraniline molecule, substituted by alkyl groups *ortho* to the nitro group, is proportional to the square of the cosine of the angle by which the nitro group is twisted away from the plane of the aromatic nucleus. The extinction coefficient of the first absorption band of these substituted *p*-nitranilines was found to be proportional to the energy of mesomeric interaction.

In the nitronaphthylamines fourteen different modes of mesomeric interaction through the naphthalene nucleus are possible. From the results discussed later it seems probable that the energies of mesomeric interaction in the nitronaphthylamines may also be related to the extinction coefficients of their first absorption bands.

Before discussing the interpretation of the absorption spectra of the nitronaphthylamines the spectra of some monosubstituted naphthalene compounds and the analogous nitranilines are mentioned.

The Spectra of the Nitronaphthylamines

(1) Monosubstituted naphthalene compounds

Details of the absorption spectra of some monosubstituted derivatives of naphthalene have been collected in Table 1. The nomenclature used to designate the absorption bands is that of Clar[6] (cf Peters[7]). When a substituent is in the 1-position the p-band undergoes a larger bathochromic shift, relative to the p-band of naphthalene, than when the same substituent is in the 2-position. Also the p-band of a 1-substituted compound is usually more intense than that of the corresponding 2-isomer. When however a "powerful" electronic substituent, eg. $—NH_2$, $—NO_2$, or $—CO_2H$, is in the 1-position then the p- and α-bands merge into a single band (pα). The merged pα-band may then be less intense than the p-band of the 2-isomer but oscillator strength is probably a better criterion in such cases.

These differences between the spectra of 1- and 2-isomers of monosubstituted naphthalene compounds may be related to the greater conjugating power of the 1-position. Coulson and Longuet-Higgins[8] have defined the conjugating power of a position, in an aromatic nucleus, as β times the self polarizability of that position (β is here the resonance integral). In naphthalene the self polarizability of the 1-position is 0·443 whilst that of the 2-position is 0·405 (compared with 0·398 in benzene).

[4] W. R. Remington, *J. Amer. Chem. Soc.* **67**, 1838 (1945).
[5] B. M. Wepster, *Steric Effects in Conjugated Systems* p. 82. Butterworths, London (1959).
[6] E. Clar, *Aromatische Kohlenwasserstoffe.* Springer-Verlag, Berlin (1941).
[7] D. Peters, *J. Chem. Soc.* 646, 1993 and 4182 (1957).
[8] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A **195**, 188 (1948).

TABLE 1. MAXIMA IN THE SPECTRA OF MONOSUBSTITUTED NAPHTHALENE

Substituent	Compounds			Solvent	Ref.
	Absorption maxima (mμ)				
	β-band	p-band	α-band		
H	220	276	311	ethanol	9
	(5·0)	(3·75)	(2·90)		
1-CH$_3$	221	282	314		
	(4·85)	(3·80)	(2·58)		
2-CH$_3$	221	276	319	ethanol	10
	(4·95)	(3·68)	(2·68)		
1-OH	233	295	323		
	(4·52)	(3·71)	(3·43)		
2-OH	226	276	325	ethanol	11
	(4·86)	(3·67)	(3·27)		
1-F		277	317		
		(3·81)			
2-F		270	321	n-hexane	12
		(3·79)			
1-Cl		281	314		
		(3·90)			
2-Cl		277	317	n-hexane	12
		(3·79)			
1-I	227	287	316		
	(4·60)	(4·03)			
2-I	230	276	323	n-heptane	12,13
	(4·40)	(3·88)			
1-NH$_3^+$		278	313		
		(3·85)	(2·60)		
2-NH$_3^+$	221	276	311	ethanolic	
	(5·01)	(3·75)	(2·60)	HCl	14,9
1-NH$_2$	240	321*			
	(4·37)	(3·20)			
2-NH$_2$	237	283	339	ethanol	15
	(4·80)	(3·80)	(3·30)		
1-NO$_2$	243	331*			
	(3·94)	(3·63)			
2-NO$_2$	261	303	349	ethanol	16
	(4·36)	(3·92)	(3·42)		
1-CO$_2$H		294*			
		(3·87)			
2-CO H	234	280	333	ethanol	15
	(4·70)	(3·80)	(3·10)		
1-SO$_3$H	224	279	315		
	(4·84)	(3·80)	(2·63)		
2-SO$_3$H	227	274	316	ethanolic	
	(5·0)	(3·69)	(2·55)	HCl	11

Log E values are in parentheses. * indicates the centre of a merged pα-band.

[9] R. N. Jones, *J. Amer. Chem. Soc.* 67, 2127 (1945).
[10] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* Figs. 196, 197. John Wiley, New York (1951).
[11] C. Daglish, *J. Amer. Chem. Soc.* 72, 4859 (1950).
[12] J. Ferguson, *J. Chem. Soc.* 304 (1954).
[13] T. M. Dunn and T. Iredale, *J. Chem. Soc.* 1595 (1952).
[14] P. Ramert-Lucas, *Bull. Soc. Chim.* 17, 262 (1950).
[15] Y. Hirshberg and R. N. Jones, *Canad. J. Res.* B 27, 437 (1949).
[16] E. R. Ward and A. Hardy. Personal communication.

(2) *Spectra of the nitranilines*

Maxima occurring in the absorption spectra of the three nitranilines have been collected in Table 2. The values for ethanol solutions were collected from the literature and the spectra were measured in cyclohexane.

As neither aniline or nitrobenzene show any absorption above Log $E = 2 \cdot 0$, in the region 325–375 mμ, then the intense long wavelength absorption of the three nitranilines can be attributed to mesomeric interaction between the substituents. Using the

TABLE 2. MAXIMA IN THE SPECTRA OF THE NITRANILINES

Isomer	Absorption maxima (mμ)	
	Ethanol[5,18]	Cyclohexane
o-nitraniline	231 (4·22)	229 (4·26)
	276 (3·69)	270 (3·69)
	403 (3·72)	377 (3·70)
m-nitraniline	234 (4·20)	228 (3·86)
	374 (3·18)	346 (3·26)
p-nitraniline	229 (3·79)	228 (4·18)
	376 (4·19)	325 (4·10)

criterion previously mentioned, i.e. the intensity of the first absorption band, as a guide to mesomeric interaction the order for the three nitranilines is:

$$p > o > m.$$

This is the expected order of interaction in these compounds.[17] The first absorption band of *p*-nitraniline under goes a bathochromic shift of 51 mμ on changing from cyclohexane to ethanol.

o-Nitraniline has three absorption bands in the region measured whilst the *meta* and *para* isomers have only two. The additional absorption band in the spectrum of *o*-nitraniline is at 270 mμ. It probably arises from steric hindrance, between the adjacent nitro and amino groups, resulting in the absorption bands of aniline, nitrobenzene and possibly the forbidden band of benzene, compounded together, appearing in the spectrum of *o*-nitraniline.

(3) *The nitronaphthylamines*

Details of the maxima in the absorption spectra of the nitronaphthylamines, measured in ethanol and cyclohexane, are shown in Table 3.

Differences in the conjugative powers of the 1- and 2-positions in the naphthalene molecule have already been mentioned. In addition steric hindrance can occur between adjacent groups in the 1- and 2-, the 2- and 3-, and the 1- and 8-positions. Steric hindrance is greater in the 1- and 8-"peri" positions than in adjacent positions on the same nucleus. In fact the large nitro group, when in the 1-position, is sterically hindered even by a hydrogen atom in the 8-position.[19]

[17] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 223ff. Bell, London (1953).
[18] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, *Analyt. Chem.* 23, 1746 (1951).
[19] A. Fischer, W. Mitchell, G. S. Ogilivie, J. Packer, J. E. Packer and J. Vaughan, *J. Chem. Soc.* 1426 (1958).

In the homonuclear nitro-1-naphthylamines, in both ethanol and cyclohexane solutions, the intensities of the first absorption bands fall in the order:

$$4 > 2 > 3,$$

(where the number indicates the position of the nitro group). This is the same sequence as was observed for the nitranilines. Where the substituent groups are in different nuclei the intensity of the first absorption band gives the order of mesomeric interaction as:

$$7 > 5 = 6 > 8.$$

In fact 7-nitro-1-naphthylamine has a more intense first absorption band than 3-nitro-1-naphthylamine. The very low absorption of 8-nitro-1-naphthylamine is not surprising because solid models (Catalin) suggest that both the nitro and amino group are twisted away from the plane of the aromatic nucleus by 80–90.°

Thus the overall series for mesomeric interaction in the nitro-1-naphthylamines, from the intensities of their first absorption bands, is:

$$4 > 2 > 7 > 3 > 5 = 6 > 8.$$

TABLE 3. MAXIMA (mμ) IN THE SPECTRA OF THE NITRONAPHTHYLAMINES

(a) *The X-nitro-1-naphthylamines*

X	Ethanol		Cyclohexane		Difference, Δλ
2	222	(4·38)	221	(4·41)	1
	278	(4·22)	272	(4·14)	6
	428	(3·95)	404	(3·87)	24
3	224	(4·47)	221	(4·48)	3
	275	(4·10)[a]	265	(4·10)	10
	416	(3·43)	382	(3·54)	34
4	260	(4·00)[a]	251	(4·21)	9
	430	(4·25)	377	(4·07)	53
5	272	(4·01)	265	(4·06)	7
	336	(3·34)	340	(3·32)	4
	416	(3·34)	385	(3·43)	31
6	222	(4·47)	220	(4·54)	2
	296	(4·25)	280	(4·33)	16
	412	(3·35)	385	(3·47)	27
7	224	(4·50)	222	(4·53)	2
	288	(4·28)	277	(4·37)	11
	436	(3·62)	401	(3·65)	35
8	232	(4·23)[b]	229	(4·28)	3
	266	(3·88)[b]	259	(4·13)[b]	7
	332	(3·46)	330	(3·48)	2
	400	(3·21)	384–396	(3·30)	ca. 10

(b) *The Y-nitro-2-naphthylamines*

Y	Ethanol		Cyclohexane		Difference, $\Delta\lambda$
1	231	(4·56)	232	(4·56)	1
	262	(4·22)	261	(4·16)	1
	318	(3·62)	322	(3·65)	4
	419	(3·84)	396	(3·72)	23
3	234	(4·56)	232	(4·56)	2
	268	(4·27)[a]	264	(4·29)[a]	4
	330	(3·79)	320	(3·74)	10
	460	(3·29)	437	(3·25)	23
4	226	(4·58)	225	(4·56)	1
	263	(4·01)[b]	254	(4·00)[b]	9
	406	(3·51)	383	(3·50)	23
5	233	(4·45)	229	(4·44)	4
	274	(4·28)	268	(4·32)	6
	344	(3·56)	334	(3·54)	10
	397	(3·31)[b]	372	(3·42)[b]	25
6	234	(4·56)	226	(4·51)	8
	258	(4·13)[b]	258	(4·23)[b]	0
	294	(3·80)	280	(4·07)	14
	405	(4·15)	365	(4·13)	40
7	230	(4·41)	226	(4·40)	4
	270	(4·34)	268	(4·34)	2
	296	(4·25)	284	(4·23)	12
	410	(3·04)	380	(3·13)	30
8	234	(4·32)	234	(4·65)	0
	272	(4·21)	258	(4·24)	ca. 10
			266	(4·23)	
	430	(3·69)	392	(3·70)	38

[a]denotes the approximate centre of a split peak.
[b]denotes a minor maximum.

The order of interaction moments, from dipole moment measurements of the nitro-1-naphthylamines in benzene,[20] is:

$$4 > 2 > 7 > 3 = 5 = 6 > 8.$$

The interaction moments of 3-, 5-, and 6-nitro-1-naphthylamine all lie within 0·02 D. of each other and as this value is within the experimental error of the method these isomers can be considered to have equal moments. These series for mesomeric interaction are in some measure of agreement with the classical structures that can be written for excited states of the nitronaphthylamines, eg. a *para* quinonoid structure for 4, an *ortho* quinonoid for 2, an *ortho–para* quinonoid for 7, and a doubly *ortho* quinonoid structure for 5-nitro-1-naphthylamine.

The nitro-2-naphthylamines form a less satisfactory series in that the spectra and dipole results do not agree so well. In the homonuclear nitro-2-naphthylamines the intensities of the first absorption bands are in the order:

$$1 > 4 > 3.$$

4-Nitro-2-naphthylamine is a *meta* compound and the low double bond order of the 2,3-bond in naphthalene is in agreement with the low mesomeric interaction indicated for 3-nitro-2-naphthylamine.

The nitro-2-naphthylamines in which the substituent groups are in different nuclei form the series:

$$6 > 8 > 5 > 7$$

for the intensities of their first absorption bands. Indeed 6-nitro-2-naphthylamine has a more intense first absorption band than 1-nitro-2-naphthylamine. The complete order of mesomeric interaction in the nitro-2-naphthylamines, as judged by the intensity of their first absorption bands is thus:

$$6 > 1 = 8 > 4 > 5 > 3 > 7.$$

The order of interaction moments, from dipole moment measurements of the nitro-2-naphthylamines in benzene,[20] is

$$7 > 1 = 8 > 6 > 5 > 4 > 3.$$

The main difference between these two series for the nitro-2-naphthylamines is the position of 7-nitro-2-naphthylamine. On the basis of classical structures a doubly *para* quinonoid structure can be written for 6, an *ortho* quinonoid for 1, and an *ortho–para* quinonoid structure for 8-nitro-2-naphthylamine. A quinonoid structure cannot be written for 7-nitro-2-naphthylamine and hence the large interaction moment for this compound is surprising.

In cyclohexane the first absorption band of *o*-nitraniline is at a considerably longer wavelength than the corresponding band for the other two isomers. A similar situation is found with 2-nitro-1-naphthylamine and 3-nitro-2-naphthylamine. It seems that when two groups which interact are adjacent on an aromatic nucleus then less energy is required to reach the first excited state. Such an effect is easily masked by solvation in a polar solvent.

By analogy with *o*-nitraniline sterically hindered 2-nitro-1-naphthylamine would be expected to show some evidence of a "break through" spectrum of 1-naphthylamine and/or 2-nitronaphthalene. In cyclohexane 2-nitro-1-naphthylamine has a broad absorption band with a maximum at 272 mμ and extending to 320 mμ (3-and 4-nitro-1-naphthylamines have narrower absorption bands at 265 and 251 mμ respectively). This broad band extending to 320 mμ may be evidence for a "break through" of the spectrum of 1-naphthylamine (maximum at 321 mμ) but not that of 2-nitronaphthalene (maximum at 349 mμ). A similar situation is found in the homonuclear nitro-2-naphthylamines. The 1- and 3-nitro-2-naphthylamines have absorption peaks at 318 and 330 mμ respectively whereas 4-nitro-2-naphthylamine shows no absorption in this region.

Solvent effects

The first absorption band, that due to mesomeric interaction, undergoes a batho-chromic shift on changing from a non-polar to a polar solvent. In Figs. 1 and 2

this shift, $\Delta\lambda$, has been plotted against the intensity of the first absorption band, Log E, a probable measure of mesomeric interaction, for the nitro-1- and 2-naphthylamines respectively.

For the nitro-1-naphthylamines a reasonable straight line can be drawn through six of the seven points indicating that solvation is related to the development of partial charges, i.e. mesomeric interaction, in these molecules. The value of $\Delta\lambda$ for 2-nitro-1-naphthylamine is only 24 mμ whereas from its extinction coefficient it should be about
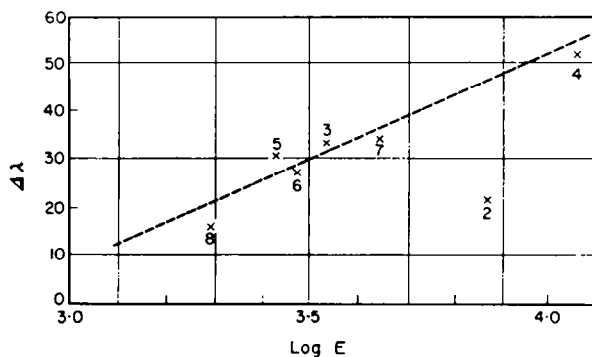
FIG. 1. Solvation of the nitro-1-naphthylamines.
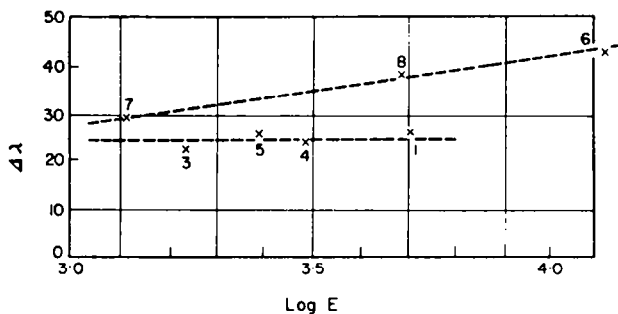
FIG. 2. Solvation of the nitro-2-naphthylamines.

45 mμ. This low value can be ascribed to the intramolecular hydrogen bonding of an oxygen atom of the nitro group with a hydrogen atom of the adjacent amine group.

Fig. 2 shows that the nitro-2-naphthylamines do not form such a well defined series as the nitro-1-naphthylamines. A possible means of correlating the results for the nitro-2-naphthylamines is indicated on the diagram. Thus solvation may be proportional to mesomeric interaction in the 6-, 7-, and 8-nitro-2-naphthylamines but the other isomers may be solvated to the same extent as the intramolecular hydrogen bonded isomer, 1-nitro-2-naphthylamine. An infra-red study by Hathway and Flett[21] suggests that intramolecular hydrogen bonding is present in both 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine; the former being more strongly hydrogen bonded than the latter. In the case of 1-nitro-2-naphthylamine the nitro group is sterically hindered by the 8-position hydrogen atom which may result in a weakening of the hydrogen bonding in this compound.

[21] D. E. Hathway and M. St. C. Flett, *Trans. Faraday Soc.* **45**, 818 (1949).

It would seem that as mesomeric interaction increases, the partial charges on the substituent groups increase, thus binding the solvent molecules more strongly into the system. Such partial charges are able to develop better in the 1-position of naphthalene due to the greater polarizability of the molecule from this position. Some recent nuclear magnetic resonance studies give a similar picture of solvation for substituted fluorobenzenes.[22]

EXPERIMENTAL

The ultra-violet absorption spectra were measured on a Unicam SP 500 photoelectric spectrophotometer. Commercial absolute ethanol was purified by filtration through silica gel and subsequent distillation. Cyclohexane was B.D.H. Spectroscopic Grade. The nitranilines were purified by recrystallization. Pure samples of the fourteen nitronaphthylamines were supplied by Dr. E. R. Ward.

[22] R. W. Taft, R. E. Glick, I. Fox, S. Ehrenson and I. C. Lewis *J. Amer. Chem. Soc.* **82**, 756 (1960).