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AZO-HYDRAZONE TAUTOMERISM IN AZO DYES. I. A COMPARATIVE STUDY OF 1-PHENYLAZO-2-NAPHTHOL AND 1-PHENYLAZO-2-NAPHTHYLAMINE DERIVATIVES BY ELECTRONIC SPECTROSCOPY†

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SUMMARY

Derivatives of 1-phenylazo-2-naphthol have been the subject of research for nearly a century, and their tautomeric behaviour is now well understood. This contrasts with sparse and controversial reports on the structure of naphthylamine analogues. To remedy this situation, a comparative study, involving compounds from both phenylazo-naphthol and naphthylamine series with OMe, CN and NO_2 *substituents in the 4' position has been started. HMO calculations indicated that the azo form of 1-phenylazo-2-naphthylamine is significantly more stable than the hydrazone, whereas the* π *bonding energies of the corresponding naphthol tautomers are of comparable magnitude. The validity of the Hückel calculations was checked on a greater set of phenylazo dyes with different coupling components. Results from electronic absorption spectroscopy show a frozen equilibrium with naphthylamine derivatives. From a McRae type analysis of the solvent-induced frequency shifts in various media an argument for the azo structure of all investigated 1-phenylazo-2-naphthylamines could be obtained. PPP calculations of spectral properties support this assignment.*

1. INTRODUCTION

One of the necessary structural conditions for a prototropic equilibrium in azo dyes is the presence of at least one protic donor group in conjugation to the azo bridge. This is a hydroxy or an amino group in most commercial dyes, and

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† The contents of this paper were part of a lecture, held at the 7th International Colour Symposium, Interlaken, on 25th September 1979. The subject matter has since been considerably revised and enlarged for publication.[32,33]

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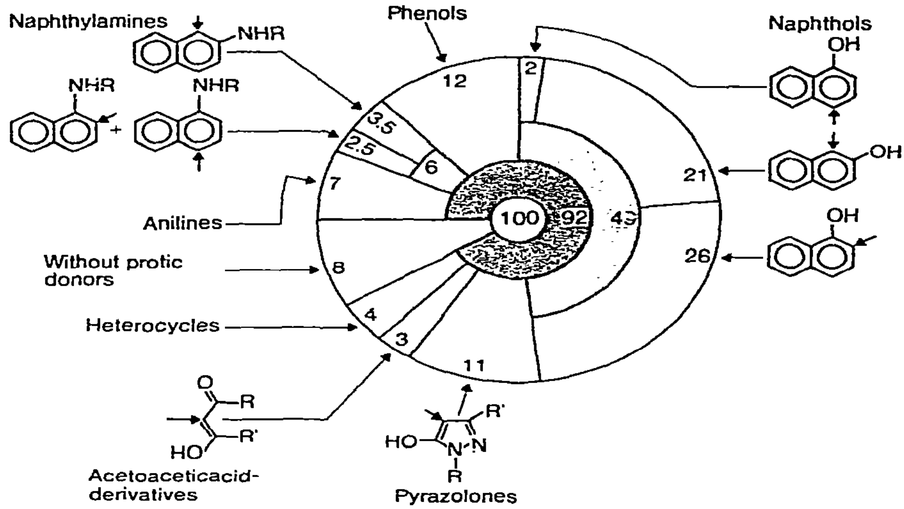


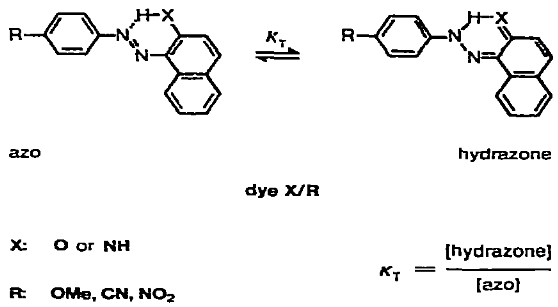
Fig. 1. Relative frequency distribution of monoazo dyes with respect to coupling component types. Coupling site (arrows) and the conjugated protic donor group are shown. Other possible substituents have been omitted from the diagram for clarity. Based on structures from ref. 1.

the equilibrium is generally referred to as the azo-hydrazone tautomerism. The very fact that donors in the coupling component enhance the reaction rate of azo coupling, makes these compounds the main source of this tautomeric structural requirement. A crude statistical evaluation of documented monoazo dyestuff structures[1] with respect to the coupling component types shows that a protic donor is nearly always present in this moiety of a technical dye (Fig. 1). Only 8% of all listed dyes are free from such substituents in the coupling part of the molecule.

With the residual 92%, a tautomeric equilibrium is at least formally possible and the tautomeric constant, K_T, will depend on the free energies of the participating species. A mobile equilibrium will only be obtained if these do not differ greatly. For big differences in the free energy content, the more stable form alone will determine the structure. The free energy of the species in question depends not only on the chemical bonding energy, but also on the solvation and association energies pertinent to the medium in which the molecule is embedded.

The question arises as to which of the tautomers is predominant in a given environment, for it can be expected that technological properties will also depend on K_T.

It is interesting to note that the dyestuff classes to which the title compounds belong are of different technical significance, as judged from their percentage



Scheme 1

in Fig. 1. Thus, dyes with naphtholic coupling components comprise nearly half of the structures (49%) whereas the related naphthylamines amount to 6% only.

An equilibrium between tautomeric azo dye species, like those shown in Scheme 1, was first suggested nearly a century ago by Zincke and Bindewald.[2] The studied compounds were phenylazonaphthol dyes. Since then, arylazo-naphthols have been investigated by various techniques in great detail.[3]

Much less attention has, however, been paid to the tautomerism of structurally similar arylazo-naphthylamine derivatives. Whereas azo structures seem to be generally accepted for the 1-phenylazo-4-naphthylamines,[3] a controversy exists concerning the structure of the isomeric 2-naphthylamine derivatives. Martynoff[4] expressed the view in the early 1950s that these dyes are fixed in the azo form, while Skulski[5] opted for a fixation of the equilibrium on the hydrazone side some 13 years later.

A mobility of the equilibrium was not observed by the authors mentioned and the presented experimental material did not establish the structure of the dyes beyond any doubt. These facts prompted us to undertake a comparative study of the six dyes, **X/R** in Scheme 1, arising from the possible combinations of the substituents X and R.

We now report our results from measurements of electronic spectra in solution together with some quantum chemical calculations.

2. EXPERIMENTAL

All compounds were prepared by known routes and were recrystallized until chromatographic purity (by t.l.c.) was attained. Satisfactory analyses were obtained and the melting points agreed with literature values.

The spectra were recorded at room temperature using either a Cary-118 or a Varian Techtron-635 spectrophotometer. Solvent origin and purity are given later in Table 1, concentration and path length in the footnotes to Tables 2 and 3.

3. APPLICATION OF THE HMO-THEORY TO TAUTOMER STABILITY

Quantum chemical calculations, even the most sophisticated ones, have not been successful in predicting tautomeric constants of relatively small molecules

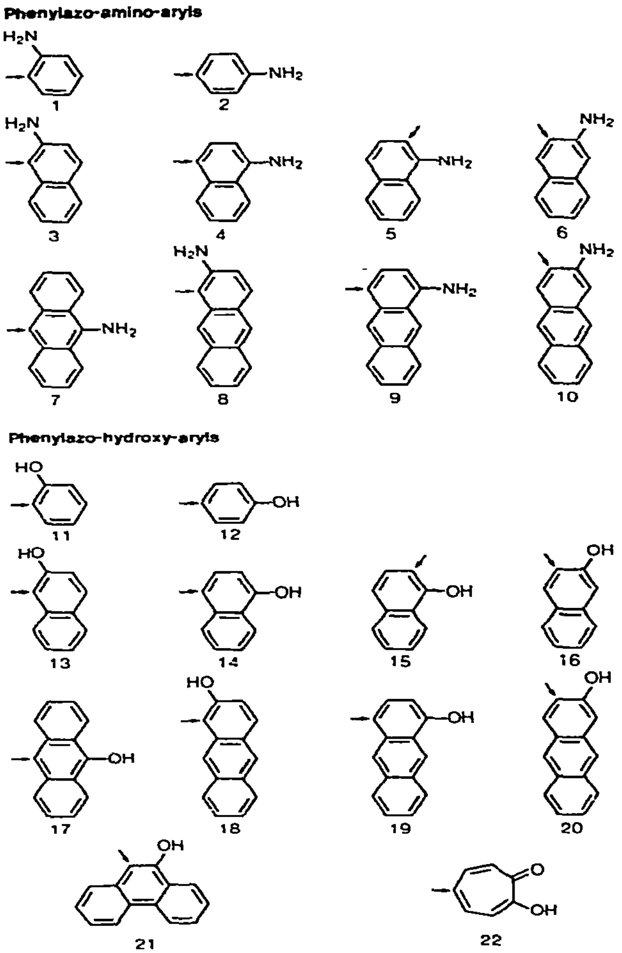


Fig. 2. Calculated dyestuff structures. The arrows indicate phenylazo groups. The formulae are shown as azo tautomers for convenience with no implications concerning the equilibrium position. Phenylazo-hydroxy-aryls are included from ref. 7.

like hydroxypyridines.[6] This is probably due to the great dependence of the tautomer energy on molecular environment. In many cases, solvation and association energies outweigh those of chemical bonding.[6] With arylazophenols, naphthols and anthrols, however, simple HMO calculations have proved useful in reproducing experimentally observed trends, as has been demonstrated by Kuder.[7]

We extended the range of these calculations to arylazo-amino-aryls. To show the reliability of the method, arylazo derivatives of acetoacetanilides, diketones, pyrazolones and some other heterocycles, for which experimental data could be located, have also been considered. The calculated structures are listed in Fig. 2.

The π bonding energy ($E_{\pi b}$) is a measure for the stability of a species within the framework of the HMO theory and can be calculated directly from Eqn (1).

$$E_{\pi b} = \Sigma b_i \alpha_i - E_\pi \tag{1}$$

Here E_π is the total π electron energy,[8] b_i is the number of electrons contributed by atom i to the π system and α_i is the Coulomb integral for atom i. The summation is taken over all atomic centres. $E_{\pi b}$ is useful in comparing tautomeric pairs or a set of structures with the same number (n) of π electrons. For π systems of different sizes, however, the *difference in π bonding energy per π electron*

$$\Delta(E_{\pi b}/n)_{A\text{-}H} = (E_{\pi b}/n)_A - (E_{\pi b}/n)_H \tag{2}$$

will measure the relative stability of the tautomers. The indices A and H refer

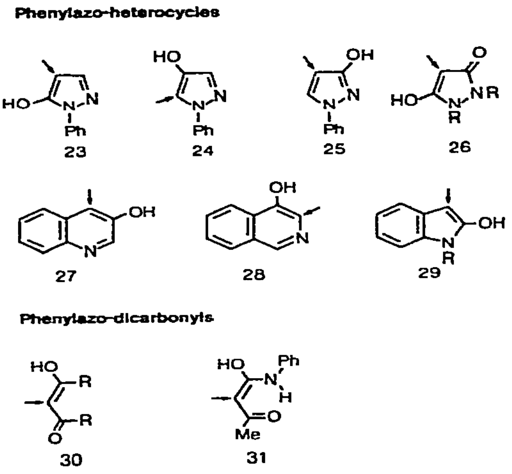


Fig. 2—*contd.*

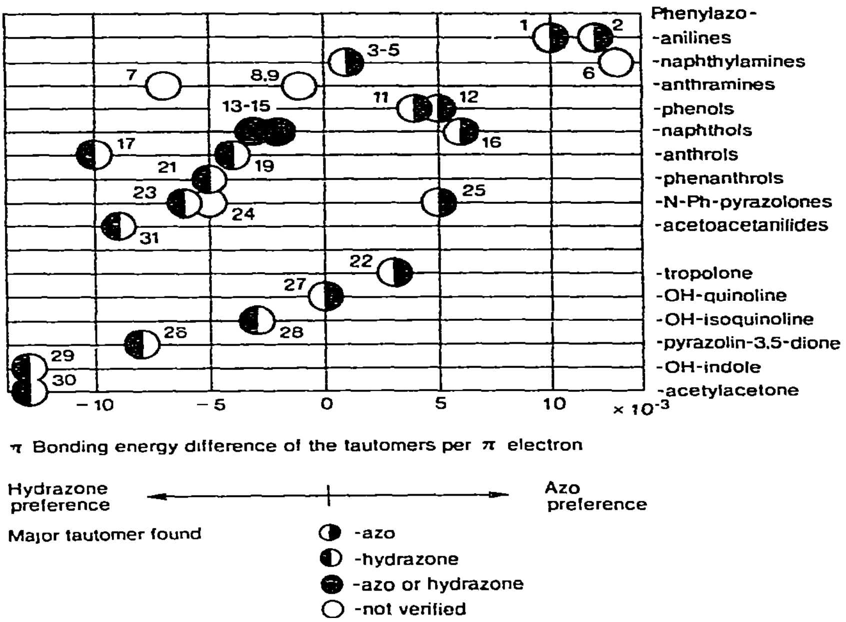


Fig. 3. A comparison of the theoretical π bonding energy difference between azo and hydrazone structures with the major tautomer found in experiment. The superscript numbers refer to the dyes in Fig. 2 and to the following literature on experimental results: (1) N-acetamides: L. Skulski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **14,** 29 (1966). (2) L. Skulski, W. Waclawek and A. Szurowska, ibid., **20,** 463 (1972). (3) This work. (4) I. Ya. Bershtein and O. F. Ginzburg, *Russ. Chem. Rev.*, **41,** 97 (1972); A. G. Catchpole and R. A. Knaust, *J. Chem. Soc.*, 4241 (1960); D. A. Ibbitson, P. C. James and R. A. Knaust, ibid., 5163 (1961). (11)–(21) J. E. Kuder, *Tetrahedron*, **28,** 1973 (1972) and references cited therein. (22) J. Griffiths, *J. Chem. Soc.*, Sect. B, 801 (1971). (23) R. A. Parent, *J. Soc. Dyers Colour.*, 368 (1976) and references cited therein; ibid., 371 (1976). (25) F. A. Snavely and C. H. Yoder, *J. Org. Chem.*, **33,** 513 (1968); C. H. Yoder, R. C. Barth, W. M. Richter and F. A. Snavely, ibid., **37,** 4121 (1972). (26) F. A. Snavely and C. H. Yoder, ibid., **33,** 513 (1968). (27)–(28) B. E. Zaitsev, G. V. Sheban, N. A. Andronova and K. M. Dyumaev, *Khim. Geterotsikl. Soedin.*, 1522 (1974). (30) H. C. Yao, *J. Org. Chem.*, **29,** 2959 (1964); F. A. Snavely and C. H. Yoder, ibid., **33,** 513 (1968); V. N. Drozd, V. I. Sheichenko and V. N. Postnov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1888 (1965). (29) F. A. Snavely and C. H. Yoder, *J. Org. Chem.*, **33,** 513 (1968). (31) B. L. Kaul, P. M. Nair, A. V. Rama Rao and K. Venkataraman, *Tetrahedron Lett.*, 3897 (1966); V. N. Drozd, V. I. Sheichenko and V. N. Postnov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1888 (1965); Y. Yagi, *Bull. Chem. Soc. Japan*, **36,** 487, 492, 500, 506, 512 (1963).

to the respective tautomers. The heteroatom parameters are described in the Appendix and the results are illustrated in Fig. 3.

It was found experimentally that in apolar hydrocarbon solvents the major tautomer in phenylazo naphthols can have both forms: hydrazone in the 2-phenylazo-1-naphthol[9,10] and azo in the 1-phenylazo-2- and 4-naphthol.[9,11–14] The equilibrium in these dyes is mobile and can easily be shifted by solvent effects.[9,12,15,16] The free energy of the tautomers must therefore be of comparable magnitude. For example, the enthalpy difference between the two tautomers of 1-phenylazo-4-naphthol in methylcyclohexane has been reported to be $2\pm0{\cdot}2$ kcal mol^{-1}.[14] Taking the average position of these naphthols as the experimentally adjusted zero point on the $(\Delta E_{\pi b}/n)$ scale, all dyes to the left of this point should be preferentially in the hydrazone form whereas those on the right hand side should show azo predominance. The available experimental evidence, as indicated in Fig. 3 is in accord with this theoretical prediction.

The influence of substituents on the equilibrium can be estimated in an inductive model.[7,17] HMO-calculations were carried out for the parent compounds, phenylazo-2-naphthol and phenylazo-2-naphthylamine, for which the electronegativity of the substituent-bearing carbon (i) atom has been varied. Accordingly, the Coulomb-integral (α) becomes $\alpha_i=\alpha+h_i\beta$, thus accounting for electronegativity perturbations (h_i) in units of the (negative) resonance parameter β.[8b] Positive h_i values were assigned for acceptor and negative values for donor substituents. The absolute value of h is assumed to be proportional to the substituent strength. Repeated calculations of π bonding energy differences with varying h yielded curves which are characteristic of the substituent effect on the tautomeric equilibrium for all accessible positions of both parent compounds. The results of naphthols and naphthylamines show close similarities. Since only the trends can be interpreted safely, the results reproduced in Fig. 4 will suffice for both classes. The actual calculations are based on parameters for the naphthol derivates.

It is interesting to note that with increasing acceptor strength of the substituents in the 2′ and 4′ positions the equilibrium shifts to the H-side. This has been found experimentally to be the case with 1-phenylazo-2-naphthols.[9,11,18] A similar trend was also observed with 1-phenylazo-4-naphthols.[12,13,16,18] On the other hand, an acceptor in the 4 position shifts to A. The 4-aza derivative (No. 27 in Fig. 2) serves as an illustration for which the azo form has been found.[19] An aza nitrogen is equivalent to an acceptor group. The 3′ position is, as expected, rather inactive but acceptor substituents in 3 yield a hydrazonic shift. Therefore, with the arylazo-2-naphthol-3-carbonamides (Naphthol AS dyes), for example, we expect a greater stability for the hydrazone form. This result is also confirmed by uv spectroscopy.[20]

As will be shown presently, all phenylazo-2-naphthylamines at hand have the azo structure under the conditions investigated. This is precisely what our HMO calculations predict. Furthermore, it follows from our estimation of substituent effects, that the best chances, if any, to detect a mobile equilibrium with the investigated naphthylamines, will be with acceptor substituted derivatives like **NH/CN** or **NH/NO$_2$** where the strong acceptor in the 4′ position will lower $\Delta E_{\pi b}$ the most.

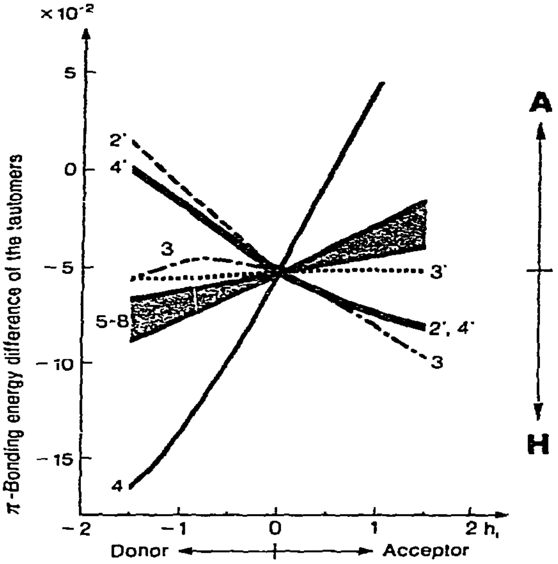


Fig. 4. Calculated substituent effect on tautomer energy difference for various positions in 1-phenylazo-2-naphthol.

4. ELECTRONIC ABSORPTION SPECTRA

The absorption spectra of the six compounds in Scheme 1 have been investigated in different media. One set of solvents was selected with nearly identical refraction indices (n_D), but widely varying permittivities (*iso-refractive* solvents). The greatest difference in n_D does not exceed 0·008 while the permittivities (D) range from 2 to over 190. Measuring spectra in binary mixtures of water with a protic or aprotic organic co-solvent, like the lower aliphatic alcohols, DMSO or DMF, has proved convenient in probing the mobility of a tautomeric equilibrium.[10,21] The second set of solvents comprises therefore ethanol–water binary mixtures. Origin and relevant properties of solvents are listed in Table 1, spectroscopic results in Tables 2 and 3.

In connection with 1-phenylazo-2-naphthol derivatives it has been claimed that the hydrazone is favoured in polar solvents.[3,10,18] More specifically, Burawoy *et al.* stated a parallelism between hydrazone stabilization and solvent permittivity,[9] although a closer look at their data for neat solvents does not justify this. Thus, for 1-(4-methoxy-3,5-dimethylphenylazo)-2-naphthol they find a lower azo/hydrazone ratio in $CHCl_3$ (0·764) or AcOH (0·570) than in pyridine (1·15), ethanol (1·13) or nitrobenzene (1·04) respectively, whereas the

TABLE 1

SOLVENT PROPERTIES

Solvent	*Symbol*	*Origin, Purity*	n_D^{20}[a]	D[b]	$\mu \times 10^{30}$[c]	E_T[d]
Cyclohexane	CH	*Fluka*, for UV	1·4262	2·02 (20°)	0	31·2
1,4-Dioxane	DIOX	*Merck*, Uvasol	1·4224	2·21	1·5	36·0
Dichloromethane	DCM	*Merck*, p.a.	1·4242	8·93	5·17	41·1
N,N-Dimethylformamide	DMF	*Fluka*, for UV	1·4269 (25°)	37·0	12·88	43·8
Propylene-carbonate	PCA	*Fluka*, purum	1·4209	65·1	16·7	46·6
N-Methylacetamide	MAC	*Fluka*, purum	1·4286 (28°)	191·3 (32°)	14·65	52·0
Ethanol[e]	EtOH	*Merck*, Uvasol	1·3614	24·55	5·77	51·9
Ethanol–H_2O (1 : 1)[e]			1·3578[f]	54·3[f]		

[a] Refractive index at the average D-line of sodium (16969 cm^{-1}) at 20°C unless followed by another temperature in parentheses.[22]

[b] Permittivity for the pure liquid at 25°C unless followed by another temperature in parentheses.[22]

[c] Dipole moment in Coulomb-meter (Cm), measured in benzene, carbon tetrachloride, 1,4-dioxan or *n*-hexane at 20°C or 30°C.[22]

[d] Dimroth's solvent polarity index. Transition energy (kcal mol^{-1}) for the long-wavelength absorption band of a standard pyridinium-*N*-phenoxide betaine dye at 25°C.[22]

[e] Ethanol used was 95%.

[f] n_D was measured with a *Zeiss* refractometer, D with a Dekameter DK 03 (manufactured by Wissenschaftlich-Technische Werkstätten, Weilheim i. OB) at 1·8 MHz, in the cell MFL 3s.

TABLE 2

ABSORPTION SPECTRA IN SOLVENTS OF CONSTANT REFRACTIVE INDEX AND DIFFERENT PERMITTIVITIES. THE NUMBERS REPRESENT λ_{max} ($\varepsilon_{max} \times 10^{-3}$) VALUES FOR THE FIRST ABSORPTION BAND[a]

X/R	*CH*	*DIOX*	*DCM*	*DMF*	*PCA*	*MAC*
O/OMe	515–520 (sh)[b]	515–520 (sh)	515–520 (sh)	515–520 (sh)	515–520 (sh)	515–520 (sh)
	454 (15·5)[b]	456 (15·4)	457 (15·0)	460 (15·6)	456 (15·3)	457 (15·4)
	434 (sh)	—	—	438 (15·4)	—	—
	415 (16·8)[b]	*416* (16·4)	*416* (15·4)	*418* (15·6)	*416* (15·9)	*417* (16·0)
O/CN	475 (19·9)	477 (22·4)	478 (23·0)	480 (20·9)	477 (22·6)	478 (21·9)
O/NO_2	476 (24·2)[c]	482 (26·4)	484 (27·7)	490 (25·0)	484 (27·6)	484 (26·6)
NH/OMe	466 (14·2)[b]	470 (sh)	465 (sh)	476 (14·6)	470 (sh)	473 (16·6)
	443 (15·6)[b]	*451* (15·4)	*447* (15·7)	*457* (14.7)	*454* (14·6)	*455* (17·0)
	426 (15·6)[b]	430 (sh)	432 (sh)	430 (sh)	433 (sh)	434 (sh)
NH/CN	471 (16·8)	477 (17·9)	477 (17·7)	492 (19·2)	484 (18·4)	489 (19·7)
NH/NO_2	487 (18·5)[d]	497 (20·2)	500 (19·7)	517 (21·7)	509 (20·8)	517 (22·0)

[a] The values refer to 5×10^{-5} mol litre^{-1} concentration and 1 cm path length, except:

[b] 1×10^{-4} mol litre^{-1}

[c] 5×10^{-6} mol litre^{-1} and $l = 5$ cm.

[d] 2×10^{-5} mol litre^{-1}.

TABLE 3

ABSORPTION SPECTRA IN ETHANOLIC SOLUTIONS. THE NUMBERS REPRESENT λ_{MAX} ($\varepsilon_{MAX} \times 10^{-3}$) VALUES FOR THE FIRST ABSORPTION BAND[a]

X/R	*EtOH—96%*	*EtOH–H_2O* (1:1)
O/OMe	520–530 (sh)[b]	
	458 (15·0)[b]	
	414 (15·6)[b]	
O/CN	478 (20·2)	
O/NO_2	483 (26·7)[c]	
NH/OMe	473 (sh)	473 (sh)
	452 (16·8)	*453* (16·2)
	428 (sh)	430 (sh)
NH/CN	488 (19·6)	489 (20·1)
NH/NO_2	514 (21·6)[d]	518 (21·7)[d]

[a] The values refer to 5×10^{-5} mol litre^{-1} concentration and 1 cm path length, except:
[b] 1×10^{-4} mol litre^{-1},
[c] 3×10^{-5} mol litre^{-1}, and
[d] $2{\cdot}5 \times 10^{-5}$ mol litre^{-1}.

permittivities increase markedly in this order (4·81, 6·15, 12·4, 24·55 and 34·82).

Of the compounds investigated only **O/OMe** showed the presence of an equilibrium. Figure 5a depicts its spectra in solvents with widely differing permittivities. One has to bear in mind that in this case the long-wavelength envelope buries at least three bands: the π,π^*-transitions of both tautomers and the n,π^*-transition of the azo group. This fact renders impossible the exact evaluation of K_T from absorption spectra. The relative amount of azo and hydrazone tautomers depends somewhat on the solvents used, as can be judged qualitatively from the relative preponderance of the two absorption regions, 400–470 nm for azo and 470–550 nm for the hydrazone form. There seems to be, however, no correlation of K_T with the permittivity, the dipole moment of the neat solvent, or with empirical polarity indices, like Dimroth's E_T-values.[22] In DCM, for example, the hydrazone content appears slightly higher than in MAC although from the permittivities (8·93 and 191·3), the dipole moments (5·17 and 14·65 Cm) and the E_T-values (41·1 and 52·0) great differences in the opposite direction would be expected.

Similarly, no correlation with permittivities of neat solvents was observed for 1-arylazo-4-naphthol disulfonic acids in a systematic study by Reeves and Kaiser.[21] They found, however, high correlation between changes in the three-dimensional structure of the solvents and the position of the equilibrium. Structural changes of the solvent can be accomplished in binary systems with one component capable of forming three-dimensional H-bonded regions

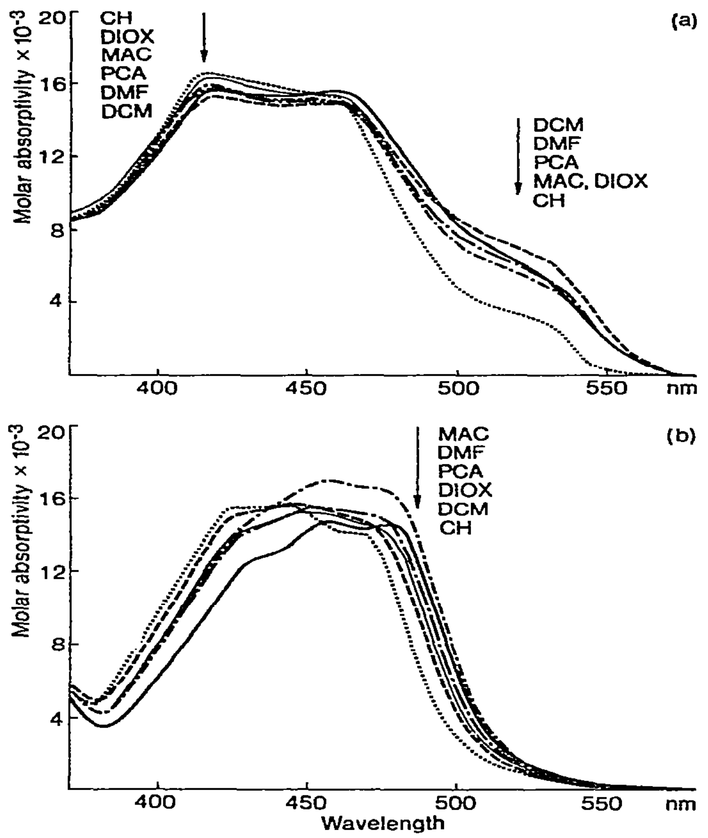


Fig. 5. Absorption spectra in neat solvents of different permittivities, (a) for **O/OMe**, (b) for **NH/OMe**.

(water, formamide), the other solvent being either two-dimensionally structured (alcohols) or aprotic. The three-dimensional solvent structures stabilize the hydrazone, whereas unstructured neat solvents or those forming two-dimensional structures favour the azo form. It is now clear that an apparent dependence of K_T on solvent permittivity applies only to those binary mixtures where the three-dimensional solvent is the more polar one. Obviously, such observations in mixtures of ethanol ($D = 24{\cdot}3$) and water (78·5) led Burawoy to the previously mentioned generalization.[9]

The spectra of **O/OMe** with fine isosbestic points in Fig. 6a show behaviour along these lines: increasing water content of ethanol promotes three-dimensional structures, thus raising K_T much more than any of the neat

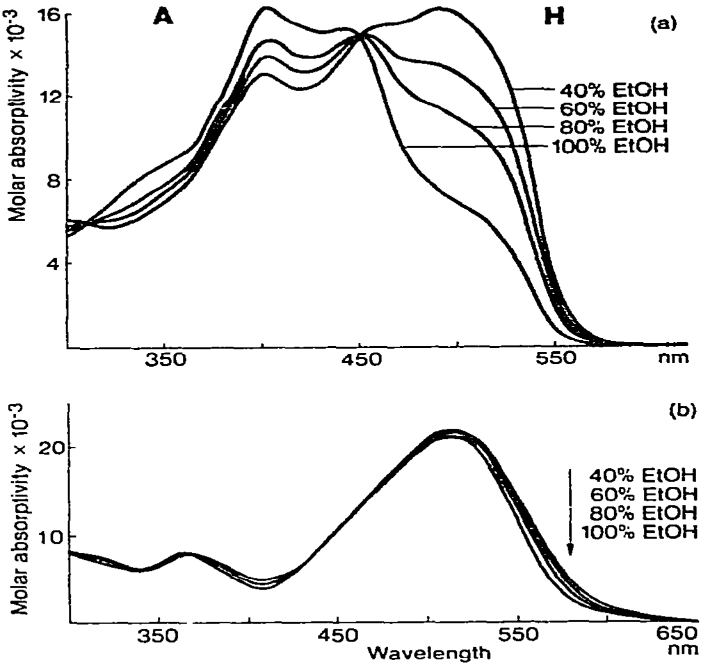


Fig. 6. Absorption spectra in EtOH-H_2O binary mixtures, (a) for **O/OMe**, (b) for **NH/NO_2**.

solvents with even greater permittivities. Similar spectra have been published for the parent 1-phenylazo-2-naphthol[10] and various sulphonic acid derivatives of 1-phenylazo-4-naphthol[21,23] in binary mixtures. With the remaining compounds in our study, we could not find any evidence for the mobility of the equilibrium under the same conditions. According to HMO calculations **NH/NO_2** is the most suitable candidate among the naphthylamines for shifting the equilibrium toward the hydrazone. Figure 6b shows that the same binaries which cause a strong shift in the case of **O/OMe**, leave **NH/NO_2** unchanged. The same is true for the other naphthylamines. Adding water to the ethanolic solution shifts the long-wavelength band slightly towards the red, but neither its shape, nor its intensity indicate a tautomeric change (*cf.* Table 3). Altering the permittivity of a neat solvent does not noticeably influence K_T of naphthylamines either, as shown for **NH/OMe** in Fig. 5b.

So far, all evidence gained from spectral data points to a frozen equilibrium with all but one of the compounds under scrutiny. Hence, the three naphthylamines and the two naphthols with electron acceptor substituents are best represented by single chemical structures. The same conclusion has also been reached for these naphthol derivatives by other authors. For **O/CN** a hydrazone content of 97% was found in $CDCl_3$, based on the ^{14}N-chemical shift in a double resonance experiment.[11] The predominance of the hydrazone was similarly established for **O/NO_2** by absorption spectroscopy.[9] No experimental proof has yet been provided, however, for the structure of the naphthylamines.

Most of the frequency shifts thus far encountered, excepting those of **O/OMe** of course, can be understood in terms of electric dipole interactions between solute and solvent, with some contributions from hydrogen bonding. An analysis of the solvent-induced frequency shifts within the framework of the McRae theory furnishes a clue to the structure of naphthylamine derivatives.

For the wave-number difference of the first electronic transition in two iso-refractive solvents i and j, the following equation can be deduced from McRae's theory:[24,25]

$$\Delta\tilde{\nu}^{(i)}-\Delta\tilde{\nu}^{(j)}=C_1\left[\frac{D^{(i)}-1}{D^{(i)}+2}-\frac{D^{(j)}-1}{D^{(j)}+2}\right]+C_2 \qquad (3a)$$

with

$$C_1=\frac{2}{hca^3}\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11}) \qquad (3b)$$

where $\mathbf{M}_{00}$ and $\mathbf{M}_{11}$ are the dipole moment vectors in the ground and first excited states of the solute, a is the *Onsager* cavity radius, h the Planck's constant and c the velocity of light. C_2 is a small term, resulting from simplifying assumptions in deriving Eqn (3), particularly from neglecting the solvent Stark effect. A similar equation was first applied by Ito *et al.* to spectra in the iso-refractive solvent pair ethylether and acetonitrile.[26] Since only two solvents were used, C_2 does not appear in their expression.

A least squares fitting of Eqn (3) to the experimental shifts was performed, taking CH as reference. The data points were taken from Table 2, and the values for DIOX have been omitted on account of the well known '*dioxan anomaly*'.[24,27] The parameters of the regression equations are collected in Table 4.

In the absence of associations due to hydrogen bonding, or other special solvent effects, a good linear correlation, with a slope proportional to $\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11})$, should result. Two observations emerge immediately: first, the correlations found for the studied compounds are only fair, thereby indicating some contributions from other than dipolar forces, inherent in Eqn 3. We attribute the major part of the deviations to H-bonding interaction as the solvents used are either proton donors (DCM), proton acceptors (PCA, DMF) or both (MAC). CH is the sole non-interacting solvent. However, great hydrogen bonding perturbations are not expected from these solvents, because they are

TABLE 4
REGRESSION PARAMETERS FOR EQUATION 3[a]

X/R	C_1	C_2	σ	r
O/CN	−197	13	60·4	0·7533
O/NO$_2$	−585	27	135·8	0·8350
NH/OMe	−884	−48	132·7	0·9200
NH/CN	−1086	−54	195·5	0·8904
NH/NO$_2$	−1571	−48	181·8	0·9500

[a] Coefficients of Eqn 3 (C_1 and C_2 in cm^{-1}) with standard deviation about the regression (σ) and correlation coefficient (r).

either weak as H-bonding partners (DCM, PCA, DMF) or self-associated (MAC).[28,29] Secondly, the slopes of the naphthylamines are generally higher than those of the naphthol derivatives. For instance, **NH/NO$_2$** is about three times more sensitive towards solvent polarity change than its naphthol analogue **O/NO$_2$**. The high C_1-value of the former could be attributed to the azo form, as it constitutes a D–Ar–A type structure, where D is an electron donor group, Ar is a conjugated π electron system and A is an electron acceptor group. Such compounds have highly polar excited electronic states of low energy and usually show large shifts with change in solvent polarity.[30] Big shifts are brought about by sizeable dipole moment increases upon excitation, rendering $\mathbf{M}_{00}$–$\mathbf{M}_{11}$, and with it C_1, significantly negative (−1571 cm^{-1} for **NH/NO$_2$**). For a comparable D–Ar–A structure, namely, for 4-dimethylamino-4′-nitrostilbene, we have calculated C_1 (−1760 cm^{-1}) from Lippert's data in ethylether and acetonitrile solvent pair,[31] taking advantage of Ito's previously mentioned approach.[26] Both values compare favourably, particularly if one considers a smaller effective cavity radius for the stilbene derivative. On the other hand, for the hydrazone **O/NO$_2$** a much smaller dipole change is expected on account of a less extended conjugation between donor and acceptor groups. This is actually reflected in the small C_1-value (−585 cm^{-1}) of this compound.

5. QUANTUM CHEMICAL CALCULATION OF SPECTRAL PROPERTIES

Pariser–Parr–Pople (PPP) type calculations have further confirmed the assignment of the azo structure to the investigated phenylazo naphthylamine derivatives. Some of the calculated spectral properties, pertinent to the first transition, are depicted in Table 5. No allowance was made to incorporate the influence of intramolecular hydrogen bridges into these calculations, but the

TABLE 5

SOME RESULTS OF PPP CALCULATIONS[a]

	Azo structure					*Hydrazone structure*				
X/R	λ_1	f_1	M_{00}	M_{11}	$\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11})$	λ_1	f_1	M_{00}	M_{11}	$\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11})$
O/OMe	443	1·067	6·0	5·0	6·7	460	0·815	12·3	33·4	−185·
O/H	435	0·922	4·7	13·3	−24·5	444	0·724	9·3	7·7	−25·6
O/CN	447	1·100	10·7	22·7	−120·	450	0·865	10·7	13·0	72·3
O/NO$_2$	453	1·017	24·0	46·0	−512·	447	0·845	21·0	19·7	27·8
NH/OMe	460	0·941	7·0	8·3	−5·6	460	0·672	8·0	31·4	−158·
NH/H	454	0·813	7·0	14·3	−41·2	446	0·607	4·0	17·3	6·7
NH/CN	465	0·983	12·7	23·0	−127·	451	0·732	7·7	9·0	100·
NH/NO$_2$	470	0·938	25·7	44·7	−480·	451	0·733	20·3	18·3	37·8

[a] Wavelength of the first transition (λ_1) in nm, its oscillator strength (f_1), and dipole moments for the ground and first excited state (M_{00} and M_{11}) in Cm × 10^{30}. The quantity $\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11})$ is given in $C^2m^2 \times 10^{60}$.

chosen geometry resembles that of a chelated structure in the *trans* configuration. Further details are given in the Appendix.

The theoretical long-wavelength band positions (λ_1) are in good agreement with the observed λ_{max} values in an apolar medium like CH (*cf.* Tables 2 and 5). The biggest differences between calculated and observed λ values have been found with the hydrazones **O/CN** (25 nm) and **O/NO$_2$** (29 nm). The oscillator strength (f_1) is large (0·7 to 1·1) for all structures, in accordance with allowed transitions, but neither these, nor the λ_1 values are suited to distinguish between the tautomeric structures. For this purpose, the whole spectrum should be compared with the predicted transitions, including the higher ones. This is done for the two nitriles in Fig. 7.

The transitions are tentatively mapped on to the absorption bands as indicated by the ascribed capital letters. The spectrum of **NH/CN** in CH agrees well with the calculated one for the azo structure but it compares poorly with the theoretical hydrazone transitions. The reverse is found for **O/CN**, although the agreement is to a lesser extent. The long-wavelength band envelope of the hydrazonic **O/CN** comprises two transitions, A and B, whereas the envelope of **NH/CN** has only one. This is also reflected in the greater half-width of the former, the difference being in the order of 800 cm^{-1} in all solvents. The other naphthylamines show a similar correspondence with calculated azo spectra.

Finally, the calculated π dipole moments sustain the conclusion drawn from solvent effects in the previous section. For the azo structures the ground state dipole moment increases from methoxy to nitro derivatives and so does the dipole change upon excitation, yielding progressively more negative $\mathbf{M}_{00}(\mathbf{M}_{00}-\mathbf{M}_{11})$. This agrees well with the order found for C_1 in the naphthylamine series (*cf.* corresponding entries in Tables 4 and 5). With the hydrazones, the

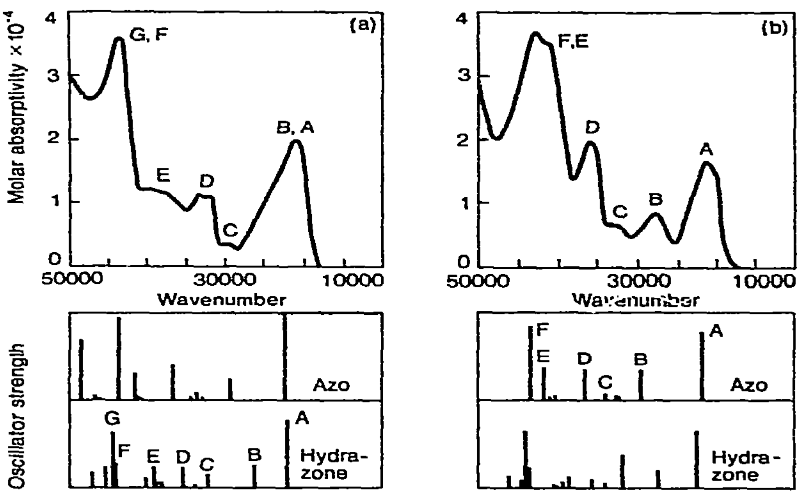


Fig. 7. Absorption spectra (in CH, top) and calculated transitions of the azo (middle) and hydrazone (bottom) tautomers, (a) for **O/CN**, (b) for **NH/CN**.

moments in both states tend to equalize if an electron withdrawing substituent is present in the phenyl moiety, thus leading to the strongly reduced sensitivity toward polarity change of the solvent.

As a consistency check, cavity radii were calculated, from eqn 3b, using C_1 from experiment and theoretical dipole moments. The obtained values range from 1·8 to 6·2 Ångstroms in the naphthylamine series. Compared to the value (8 Å) estimated for the 4-dimethylamino-4′-nitro-stilbene by Lippert,[27a] they appear to be low but certainly in the right order of magnitude. This result might indicate that either H-bonding contributions bias the value of C_1, or, our calculation slightly underestimates the dipole terms. It is known, however, that eigenvector properties, of which the dipole moment is one, depend more delicately on the parametrization than the energy terms.

6. CONCLUSIONS

The major findings of this work are: (i) according to HMO calculations, 1-phenylazo-2-naphthylamines are dominated by the azo structure, even in the presence of a strong electron acceptor group in the phenyl-moiety; (ii) the spectroscopic data in neat solvents of different permittivities, as well as those in ethanol–water binary mixtures, indicate a frozen equilibrium; (iii) this equilibrium lies on the azo side, as follows from a McRae analysis of the solvent-induced frequency shifts; and finally (iv) PPP calculations support this assignment. As the arguments used here are either theoretical in nature or rely heavily on quantum chemical methods, a more direct experimental approach is needed to supplement the conclusions arrived at in this paper. Subsequently, an account of our nmr, Raman and X-ray studies will be given.[32] Another paper will be devoted to the tautomeric properties of the title compounds under conditions relevant to industrial practice.[33]

TABLE 6

ONE-CENTRE INTEGRALS FOR THE HMO AND PPP PROCEDURES[a]

		HMO	*PPP*	
Atom i	*Valence state*	h_i	W_i	(ii, ii)
C	tr tr tr π	0	−11·42	10·84
N	tr^2 tr tr π ($\geqslant$N)	0·5	−14·1	12·3
N^+	tr tr tr π^2 (>NH)	1·5	−27·3	18·0
	(—NO_2)		−25·0	16·6
O	tr^2 tr^2 tr π (>C=O)	1·0	−17·96	15·23
	(—NO_2)		−17·1	13·9
O^+	tr^2 tr tr π^2 (—OH)	2·0	−32·9	22·9
	(—OMe)		−32·5	22·5

[a] Coulomb parameter (h_i), valence state ionization potential (W_i, eV) and one-centre electron repulsion integral (ii, ii) in eV.

TABLE 7

TWO-CENTRE INTEGRALS FOR THE HMO AND PPP PROCEDURES[a]

Bond i–j	k_{ij} (*HMO*)	β^c_{ij}(*PPP*)
C—C	1·0	−2·318
C—N	0·9	−2·318
	1·1 (>C=N—)[b]	−3·25 (—C≡N)
N—N	1·0	−2·318
C—N^+	0·7	−2·09
		−1·6 (>C—NO_2)
N—N^+	0·7	−2·09
C—O	1·0	−2·318
C—O^+	0·8	−1·8
N^+—O		−2·4 (—NO_2)

[a] Hückel resonance parameter (k_{ij}) and core resonance integral (β^c_{ij}, eV).

[b] In hydrazone fragment only.

APPENDIX

Standard Hückel and Pariser–Parr–Pople (PPP) procedures have been used.[34,35] The parameters, for both types of calculations are collected in Tables 6 and 7. The Hückel integrals $\alpha_i = \alpha + h_i\beta$ and $\beta_{ij} = k_{ij}\beta$ were chosen in such a way as to be compatible with reported calculations[7] on arylazo-hydroxy-aryls.

For the PPP calculations 25 configurations were taken into account, based on the five highest occupied and five lowest unoccupied scf-mo's. An idealized geometry was assumed throughout with bond length of 1·4 Å and bond angles of 120°. The two centre electron repulsion integrals were calculated by the Mataga-Nishimoto[36] formula.

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