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AZO–HYDRAZONE TAUTOMERISM IN AZO DYES. II. RAMAN, NMR AND MASS SPECTROMETRIC INVESTIGATIONS OF 1-PHENYLAZO-2-NAPHTHYLAMINE AND 1-PHENYLAZO-2-NAPHTHOL DERIVATIVES

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SUMMARY

In a comparative study 1-phenylazo-2-naphthylamines, **1(R)**, *and 1-phenylazo-2-naphthols,* **2(R)**, *with $R = MeO$, CN and NO_2 have been investigated by means of Raman, NMR and mass spectroscopy in order to elucidate their tautomeric structures. Based on Raman spectra obtained under resonance conditions, the* trans *azo structure has been inferred for* **1(R)** *with all the substituents under scrutiny. From the naphthol derivatives the hydrazone predominance has been confirmed for* **2(CN)** *and* **2(NO$_2$)** *in agreement with previous reports using different techniques. No useful Raman spectrum could be obtained, however, for* **2(MeO)** *due to the inherent fluorescence of this dye. Here nuclear magnetic resonance proved to be helpful, yielding a K_T of 0·7 from both ^{13}C and ^1H chemical shift arguments. For the other five dyes the Raman results have been corroborated by the measurement of carbon and proton chemical shifts [$\delta(C\text{-}2)$, $\delta(H\text{-}3)$ and $\delta(H\text{-}8)$] and the coupling constants $J(H\text{-}3, H\text{-}4)$. In the mass spectrometer all compounds behaved similarly irrespective of the tautomeric structures in solution or in the solid state with an 'azo-type' fragmentation pattern originating from a primary C—N cleavage of the molecular ion. A theoretical discussion is provided to show that this decomposition pathway for the hydrazones is not contradictory to the results obtained above. An initial C—N*

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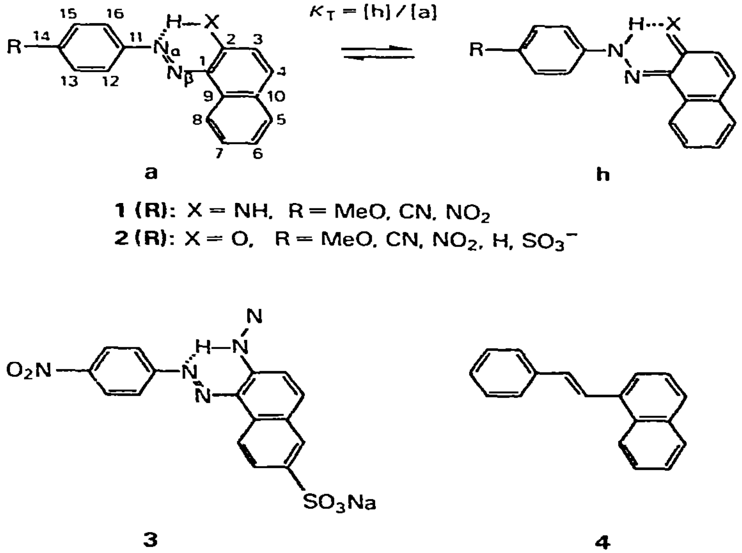
cleavage instead of the generally assumed N—N cleavage of the hydrazone molecular ion can occur in certain cases, particularly with electron withdrawing R, thus leading to the observed azo type decomposition. From the present results it became obvious that mass spectrometry is not a generally applicable tool for azo–hydrazone structure discrimination.

1. INTRODUCTION

It has been recognized that the nature of the prevalent tautomeric structure has a profound influence on the technological properties of azo dyes.[1] Investigations concerning azo-hydrazone equilibria, their environmental dependence and interrelationship with chemical constitution are therefore of prime interest in dyestuff chemistry. Previous work in this field dealt very unevenly with different azo dye structures. Phenylazonaphthols, for instance, were investigated in great depth whereas our understanding of phenylazonaphthylamine tautomerism is poor and controversial.[2] It is the aim of this paper to elucidate further the structure of 1-phenylazo-2-naphthylamine dyes **1** by comparing their spectral properties with those of the naphthol dyes **2** (Scheme 1).

By means of electronic absorption spectroscopy it could be demonstrated that neither solvent permittivity—nor solvent structure—changes can provoke a noticeable shift in the equilibrium position of dyes **1** and consequently their



1 (R): X = NH, R = MeO, CN, NO_2
2 (R): X = O, R = MeO, CN, NO_2, H, SO_3^-

Scheme 1

tautomer energies must differ significantly.[2] Hückel molecular orbital (HMO) calculations predicted the azo form to be the more stable species and arguments derived from the solvent induced frequency shifts of the absorption spectra supported the assignment of the azo structure to these compounds. Also the comparison with calculated spectral properties within the framework of the Pariser–Parr–Pople (PPP) theory led to the same conclusion.[2] As most of these deductions rely on semi-empirical concepts with their inherent approximations, further experimental verification was needed. Here we report the results of our Raman, NMR and mass spectrometric investigation.

2. EXPERIMENTAL

The dyes **1**(R) and **2**(R) (R = MeO, CN, NO_2) were the same as those in Part I.[2] Compound **3** was obtained by coupling diazotized *p*-nitroaniline on Broenner's acid and purified chromatographically.

Raman spectra in solution were recorded in a rectangular UV quartz cell of 1 cm path length (10^{-4}M in CCl_4 or H_2O) using a Jobin–Yvon–Ramanor HG.2S spectrometer with 90° illumination at ambient temperature in the wavenumber range 900–1700 cm^{-1}. Excitation at 514·5 nm (~600 mW at sample position) was with a Spectra Physics Model 171 Ar^+ laser. Spectral bandwidth was ~4 cm^{-1} for all measurements. Repeated scans showed excellent reproducibility with no sign of sample deterioration. Compound **4** was recorded in polycrystalline form on a Cary Model 83 Raman spectrometer in a non-rotating sample holder with a spectral bandwidth of 5 cm^{-1}. Excitation at 488 nm (~40 mW at sample position) was with a Lexel Model 75 Ar^+ laser.

^{1}H-NMR (100 or 360 MHz) and ^{13}C-NMR (20 or 25 MHz) spectra were recorded in $CDCl_3$ at room temperature. ^{13}C chemical shifts (in ppm from internal TMS, with assignment enclosed in parentheses) were as follows:

1(MeO)	160·6(14), 148·0(11), 138·1(2), 134·7(1), 132·9, 127·9, 127·4, 127·4, 126·8, 123·4(12), 123·1(6), 122·1(8), 119·6(3), 114·3(13), 55·5(Me)
1(CN)	156·0(11), 139·6(2), 135·6, 134·7(1), 133·2(13), 128·2, 128·2, 127·6, 127·5, 123·8, 122·3(12), 121·8, 119·5(CN), 119·3(3), 111·4(14)
1(NO_2)	157·4(11), 147·1(14), 139·9(2), 136·0, 134·7, 128·4, 128·3, 127·9, 127·5, 124·9(13), 124·0(6), 122·1(12), 121·9(3), 119·2(8)
2(MeO)	161·3(14), 160·8(2), 141·9(11), 136·7, 133·4, 129·6, 128·3, 128·2, 128·2, 124·8, 122·1, 122·1(12), 121·6, 114·8(13), 55·6(Me)
2(CN)	178·9(2), 146·6(11), 143·0(4), 133·8, 133·2, 131·6, 129·6, 129·1, 128·6, 127·3, 126·1(3), 122·3(8), 118·8(CN), 117·3, 108·5(14)
2(NO_2)	180·0(2), 148·0(11), 144·7(14), 143·5(4), 133·1, 132·1, 129·8, 129·2, 128·7, 127·6, 126·4, 125·8(13), 122·6, 116·7(12)

Low resolution mass spectra were recorded on a Varian MAT CH 7 spectrometer with coupled data system SS100 (ion source temperature: 170°C; ionisation potential: 70 eV; direct sample insertion). For the high resolution work a CEC 21-110 B instrument was used.

3. VIBRATIONAL SPECTRA

Vibrational spectroscopy is a suitable tool for differentiation between tautomeric structures but IR studies alone do not suffice in the case of azo dyes.

Systematic IR work has been published on the tautomerization of phenylazonaphthols with conflicting results.[3-5] The spectra are complex and their assignment rendered difficult because the analytically useful group vibrations are intermixed with those of aromatic rings. The latter are strong in most cases. For the azo tautomer the N=N valence and the C—N stretching mode would be of interest but these are either weak for the *trans* configuration or difficult to locate.[6] No diagnostic value could, therefore, be attributed to these absorptions in general.[3] Some effort has been made to estimate the hydrazone content of tautomeric mixtures from the intensity of the carbonyl stretching vibration[4] but the assignment of this band is controversial. Some authors connect it to the 1620 cm^{-1} region,[3-4,7] while Lippert *et al.* conclude from the measurement of ^{17}O-labelled phenylazonaphthols that carbonyl stretching should rather be assigned to the 1570 cm^{-1} range.[5] Intramolecular hydrogen bonds aggravate the situation. In **2(H)**, for example, only a modest and atypical solvent sensitivity of the C=O band position has been observed, in accordance with a strongly chelated structure.[4] As a consequence, carbonyl stretching might even appear at lower frequencies than some ring vibrations.[5] Under these circumstances, coupling between C=O stretch- and aromatic ring-vibrations cannot be excluded and the effect on carbonyl intensities becomes unpredictable.

Similarly complex are the spectra of the phenylazonaphthylamines **1** and to our knowledge no systematic IR investigation has been performed concerning their possible tautomerization.

It appears, for reasons just discussed, more promising to take advantage of the Raman effect (RE), particularly under resonance conditions.[8] Several papers have dealt with the RE of azo dyes[9-24] but most of them have ignored possible tautomerization or applied RE solely to non-tautomeric azo compounds.[9-17] Others have considered both azo and hydrazone forms together with acid–base equilibria with one of the tautomeric structures belonging usually to the conjugated acid or base of the dye.[18-24] One of the main advantages of the resonance Raman effect is the simplicity of the resulting spectra. Only vibrations characteristic for the 'chromophore' system, especially the totally symmetric ones, are enhanced.[8,25] The enhanced Raman band intensities are generally 10^2–10^6 times higher than normal

Raman lines and correspondingly the detection limits are low. This makes possible the recording of the spectra in very dilute solutions with negligible intermolecular interactions. Another field of application, barely accessible by other methods, is the use of resonance RE in tautomeric structural investigation of dyes under technologically relevant conditions, as for example on dyed textile fabrics.[26]

For the present purpose we have measured the Raman spectra of dyes **1**(**R**) and **2**(**R**) with R = MeO, CN and NO_2 using CCl_4 as solvent. No usable spectrum could be obtained for **2**(**MeO**), however, due to strong fluorescence background which most likely originated from the compound itself. The conditions for resonance RE are obviously fulfilled as the 514·5 nm Ar^+ laser excitation line lies on the long wavelength side of the maximum, well within the absorption band envelope[8] (Fig. 1)

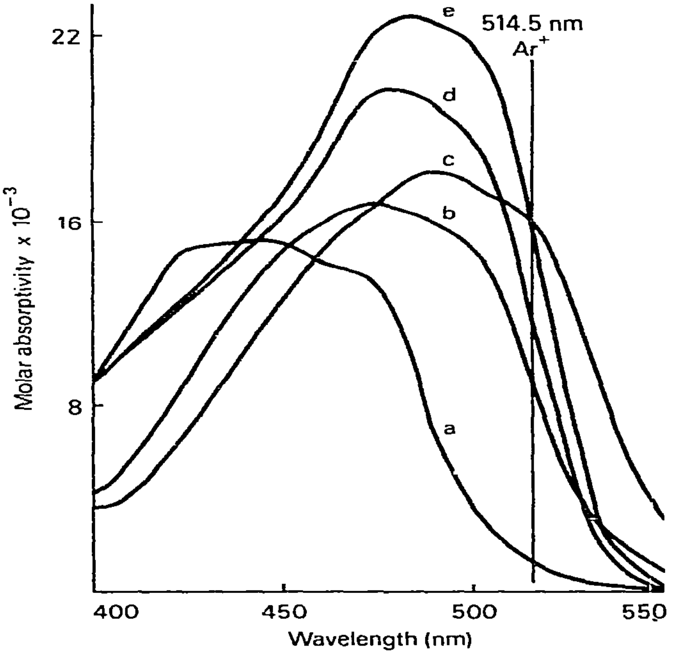


Fig. 1. Absorption spectra of dyes (a) **1**(MeO), (b) **1**(CN), (c) **1**(NO_2), (d) **2**(CN) and (e) **2**(NO_2) in CCl_4 (5×10^{-5} M).

and a concentration of 10^{-4} M together with a narrow bandwidth of 4 cm^{-1} sufficed to obtain Raman spectra of good quality.

We can subdivide the spectra according to their general appearance into two groups, with far reaching similarities within and striking dissimilarities between them. The spectra of the two naphthol derivatives **2**(CN) and **2**(NO_2) belong to the first (Fig. 2), those of the three naphthylamines to the second group (Fig. 3).

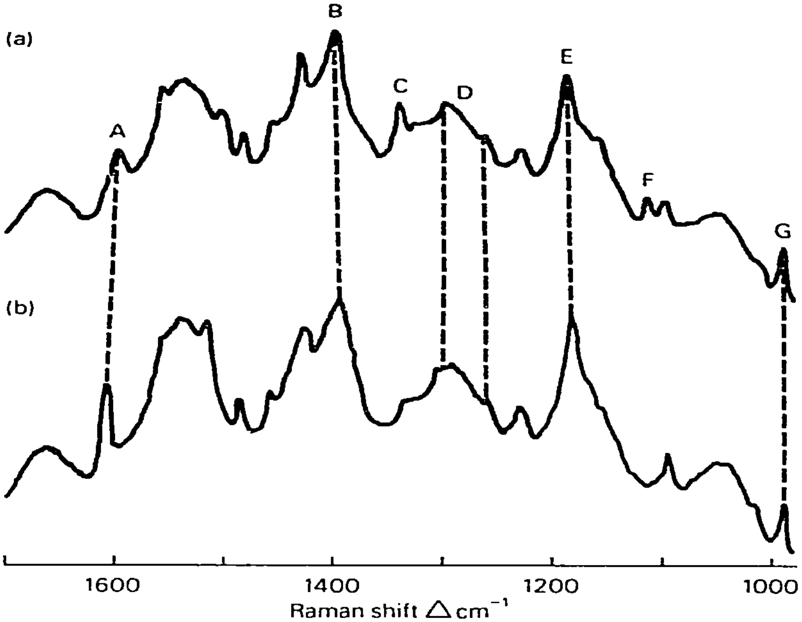


Fig. 2. Resonance Raman spectra of (a) $2(NO_2)$ and (b) $2(CN)$ (Group I) in CCl_4 (10^{-4} M). λ_{exc} = 514·5 nm.

The most remarkable feature of the Group II spectra is the predominance of a few strong bands, whereas the intensities in Group I are more evenly distributed and superimposed on a relatively strong fluorescence background. Some fluorescence is also observed in $1(NO_2)$ but practically none in the other two naphthylamines. As the background emission also persists in the solid state spectra of the well purified phenylazonaphthols,[26] it is probably correct to attribute it to the dyes themselves rather than to impurities.

The hydrazone outweighs by far the azo tautomer in 2(CN), as was established by NMR studies[27] and similarly in $2(NO_2)$ according to UV measurements.[28] Previously it was stated that the naphthylamines **1** can best be represented by one single structure.[2] These facts, together with the above mentioned dissimilarities between the groups, already suggest the predominance of the azo tautomer in the naphthylamine series. Consequently, the Group I spectra should be compatible with the hydrazone structure. A comparison with literature data helps to assign some of the observed Raman bands and will support the present argument.

The observed frequencies are collected in Tables 1 and 2 together with a summary of their assignment. Our own data are supplemented in Table 1 by those of $2(SO_3^-)$ (Orange II) and 2(H) (Sudan I) from ref. 19. These dyes show azo type spectra in alkaline solution whereas under neutral conditions hydrazone type spectra were observed.[19]

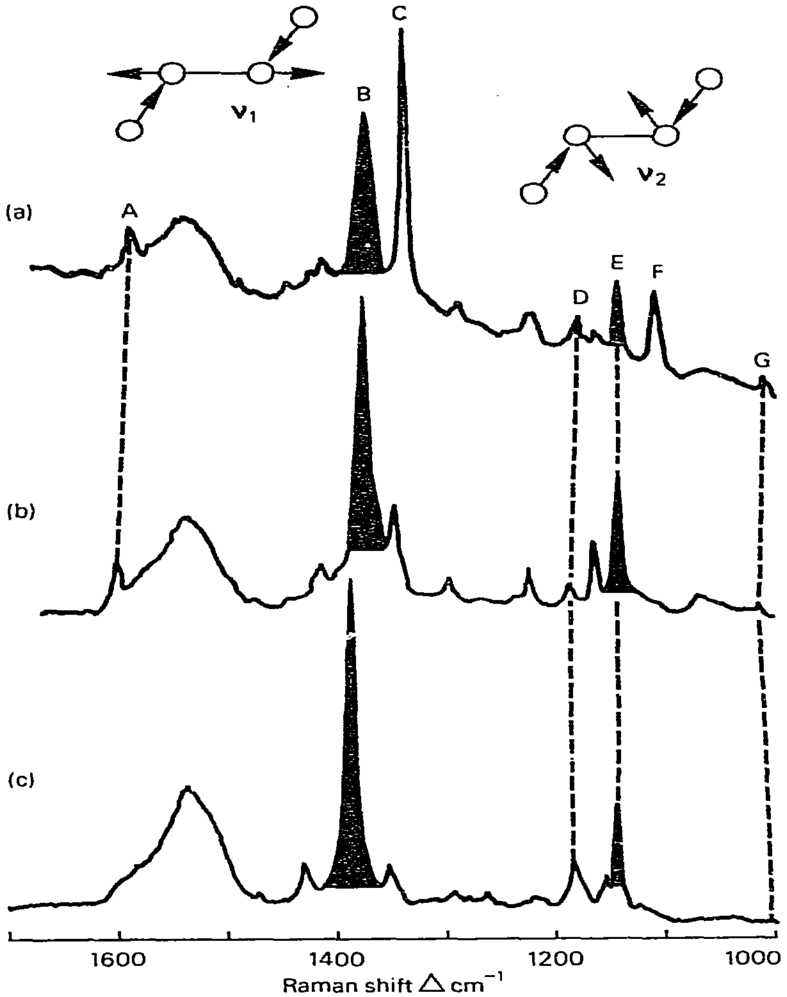


Fig. 3. Resonance Raman spectra of (a) **1**(NO$_2$), (b) **1**(CN) and (c) **1**(MeO) (Group II) in CCl$_4$ (10^{-4} M). $\lambda_{exc.}$ = 514·5 nm. The Cartesian displacement of the atoms during the fundamental vibrations of the azo linkage are shown above according to the four-mass model. The corresponding Raman bands are shaded.

3.1. *Assignment of the Group I spectra*

The two spectra in Fig. 2 show similar intensity distribution and a one-to-one correspondence of nearly all bands in the wavenumber range recorded (1700–900 cm^{-1}). The peaks C and F represent obvious exceptions and are due to the symmetrical nitro and C—N(NO$_2$) stretching modes, respectively. The ν_s(NO$_2$) vibration is usually strong in Raman as in the case of nitrobenzene,[29] and *o*- and *m*-nitroanilines respectively but weak in *p*-nitroaniline.[30] The low intensity of the

TABLE 1
OBSERVED RAMAN FREQUENCIES (cm^{-1}) OF 1-PHENYLAZO-2-NAPHTHOL DERIVATIVES AND THEIR ASSIGNMENT^a

Band	2(CN)	2(NO$_2$)	2(SO$_3^-$)^b	2(H)^c	*Assignment*
A	1610 s	1599 m	1601 s	1608 s	Benzene ring (8a, 8b)
B	1395 s	1401 s	1390 m	1396 m	Naphthalene ring
C		1342 m			$\nu_s(NO_2)$
D	1308 w				
	1294 w	1299 w	1262 w	1270 vw	ν(C—N) Hydrazone
	1260 w	1261 w			
E	1182 s	1188 s	1235 m	1236 s	ν(N—N) Hydrazone
F		1114 w			ν(C—N) Nitro
G	988 m	990 m			δ(C—H) Naphthalene ring

Solvent: ^{a} carbon tetrachloride, ^{b} water (neutral), ^{c} ethanol.

1342 cm^{-1} band of 2(NO$_2$) is therefore in accord with the substituted *p*-nitroaniline structure of the hydrazone. Conversely, the strong dominance of this vibration in the case of 1(NO$_2$) might reflect the non-hydrazone character of the latter, in agreement with its assumed azo structure. The assignment of a C—N stretching mode to F is analogous to that reported[31] for *p*-nitroaniline, which appears at 1110·9 cm^{-1}.

The origin of the broad band around 1665 cm^{-1} is obscure. Hydrazonic C=N or C=O stretching modes can probably be disregarded as no corresponding band was found in the infrared spectra though such vibrations should be IR active. This band was also absent in the 2(NO$_2$) solid state Raman spectrum.[26]

The sensitivity of band A toward ring substitution [1610 cm^{-1} in 2(CN) vs 1599 cm^{-1} in 2(NO$_2$)] points to a benzene vibration. We assign this band to the 'quadrant stretching' of the phenyl ring, derived from the benzene mode 8a, 8b in Wilson's notation.[32] The strongly asymmetric *para* substitution renders this vibration also active in IR and consequently medium intensity infrared absorptions have been found at nearly the same frequencies (1610 and 1600 cm^{-1}) in methylene chloride.

TABLE 2
OBSERVED RAMAN FREQUENCIES (cm^{-1}) OF 1-PHENYLAZO-2-NAPHTHYLAMINE DERIVATIVES AND THEIR ASSIGNMENT^a

Band	1(MeO)	1(CN)	1(NO$_2$)	3^b	*Assignment*
A		1600 w	1588 w	1588 w	Benzene ring (8a, 8b)
B	1387 vs	1374 vs	1371 vs	1381 s	ν(N=N) (ν_1)
C			1337 vs	1339 vs	$\nu_s(NO_2)$
D	1183 w	1185 w	1182 w	1175 w	δ(C—H) + ν(Ar—N=)
E	1144 m	1142 m	1141 m	1148 m	ν(Ar—N=) + δ(C—H) (ν_2)
F			1108 m	1110 m	ν(C—N) Nitro
G		1011 vw	1008 vw	1007 w	δ(C—H) Naphthalene ring

Solvent: ^{a} carbon tetrachloride, ^{b} water.

All the bands present between 1620 and 1390 cm^{-1} belong to valence modes of the benzene and the naphthoquinoid rings. Some of these are obscured by the broad and strong solvent absorption near 1540 cm^{-1}. Band B in the vicinity of 1400 cm^{-1} should be attributable to C—C stretching of the *o*-quinoid ring in analogy to reported assignment of other phenylazonaphthol dyes.[19] The C—N stretching of the hydrazone linkage is expected to appear around 1300 cm^{-1} with medium to weak Raman intensity. We observed a broad band (D) in this region with some superimposed small peaks. No detailed assignment of these is, however, possible without further costly investigation. More characteristic is probably band E arising from N—N stretching. The lower frequencies in **2**(CN) and **2**(NO_2) at 1182 and 1188 cm^{-1} as compared to those of **2**(SO_3^-) and **2**(H) at 1235 and 1236 cm^{-1} reflect the greater electron withdrawing effect of the nitrile and nitro substituents.

3.2. *Assignment of the Group II spectra*

In a simplified model of *trans*-azobenzene, with aryl groups represented by single mass points ('four-mass' model of C_{2h} symmetry), group theory predicts three totally symmetrical (A_g) normal vibrational modes, allowed and polarized under Raman conditions.[6,10] These are ν_1, ν_2 and ν_3 in Luettke's notation[6] corresponding approximately to N═N stretch, C—N stretch and in-plane deformation vibrations, respectively. In actual azo dyes the molecular symmetry is generally lower in solutions, even for azobenzene itself.[14] For the azo tautomer of the presently investigated dyes the highest symmetry attainable is C_s provided the molecule is planar and of *trans* configuration. The requirements for planarity are approximately fulfilled for **1**(NO_2) in the crystalline state as follows from crystal structure determination.[33]

Even though the overall symmetry of the molecule as such can be lower than has been considered for the four-mass model, the local symmetry in the vicinity of the azo group will be only slightly perturbed.[13] As a consequence, high Raman intensity with low depolarization ratio is expected, at least for some of the mentioned A_g modes. Hacker found intense Raman lines between 1380 and 1440 cm^{-1} for azobenzene and azonaphthalene derivatives, attributable to N═N stretching mode ν_1. The corresponding depolarization ratios were generally low (0·3 to 0·48) in agreement with the high symmetry of this vibration.[12,13]

We, therefore, assign the very prominent band in the Group II spectra near 1380 cm^{-1} (B in Fig. 3) to the same N═N valence mode. Band positions and assignment thereof are in good agreement with those reported for **2**(SO_3^-) and **2**(H) in alkaline solution.[19]

Although the most prominent Raman line in naphthalene is also confined to this wavenumber region,[34] we believe with Hacker[13] that the intensity of this ring vibration is inferior to the N═N stretching mode. This is supported by the Raman spectrum of the structurally similar styrylnaphthalene, **4** (Fig. 4), the *trans* configuration of which is ensured by the synthetic route employed.[35] The

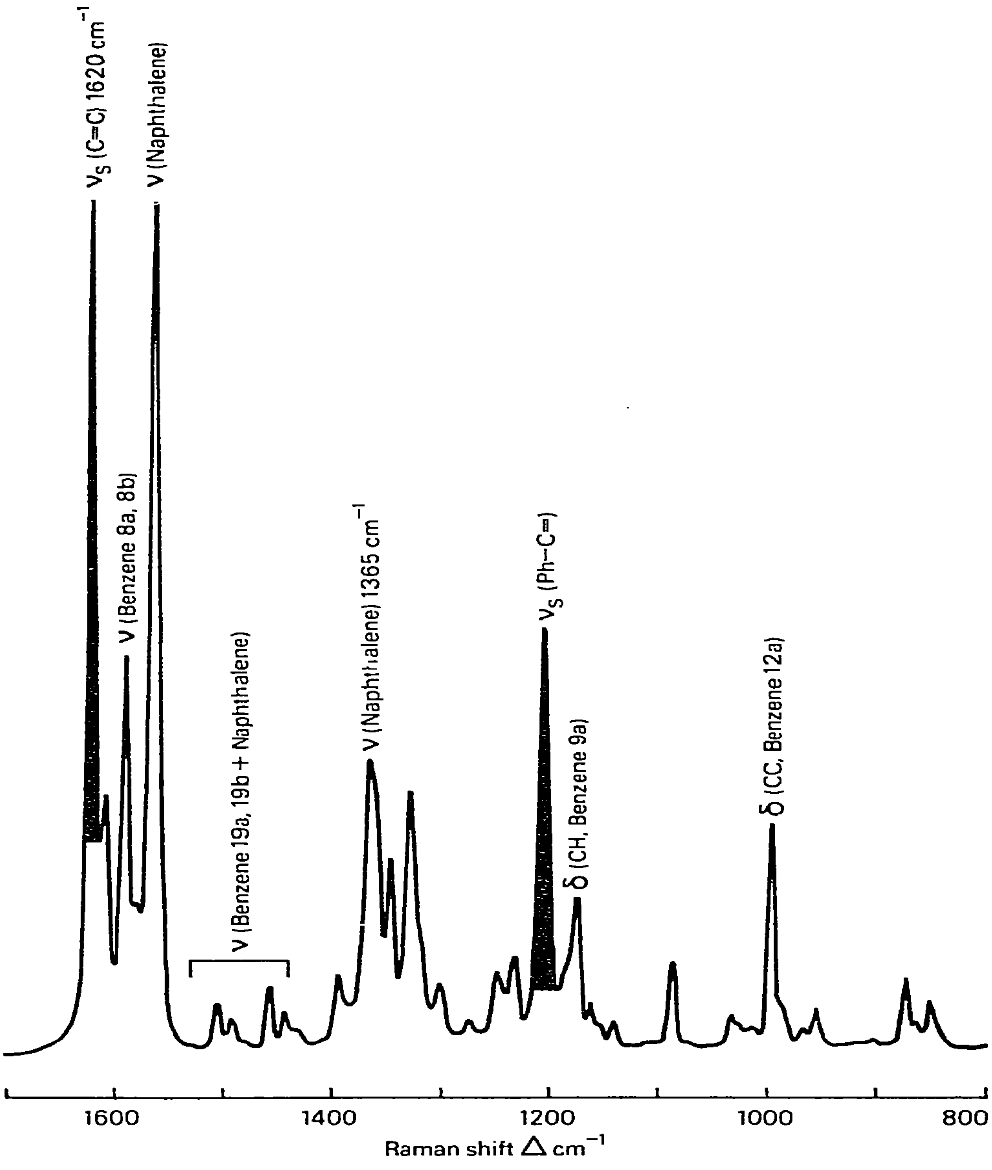


Fig. 4. Raman spectrum of 4 (polycrystalline sample). The benzene vibrations are numbered according to Wilson[32] and the shaded Raman bands correspond to modes similar in nature to ν_1 and ν_2 of the azo compounds. $\lambda_{exc.} = 488$ nm.

naphthalene ring vibration (1365 cm^{-1}) is here significantly less pronounced than the C═C stretching mode (1620 cm^{-1}) which corresponds to ν_1 of the azo dyes.

The frequency of the N═N stretching mode decreases in the order **1**(MeO), **1**(CN), **1**(NO_2) (1387, 1374 and 1371 cm^{-1}) in agreement with diminishing π-bond orders, extracted from our previously reported PPP calculations (0·802, 0·797 and 0·788 respectively[2]).

The observed low frequency for this vibration is indicative of a *trans* azo linkage. The frequency of the *cis* form should be higher, in analogy to N═N stretching of *cis*-(1511 cm^{-1}) and *trans*-(1442 cm^{-1}) azobenzene.[6] Taking into account the low frequency shift of phenylazonaphthylamines relative to azobenzene, the *cis* form of the former should appear anywhere between 1450 and 1500 cm^{-1}. Unfortunately, this region is obscured by the broad band of carbon tetrachloride. However, the sodium sulphonate **3** could be recorded in water and shows that this region is practically free of bands (Fig. 5).

The spectra of the phenylazonaphthylamines investigated herein are thus consistent with a *trans*-azo configuration. The *cis* form is probably too transient at room temperature to be observed,[36] even under laser irradiations used in this study. A high rate of thermal *cis*→*trans* reversion was reported for some substituted azo dyes,[36,37] including 1-phenylazo-2-naphthylamine.[37] Under rigorous Raman conditions, with irradiation right into the long wavelength absorption band, no photoisomerization was observed with Methyl Orange.[15] Other resonance Raman work on substituted azo dyes is in agreement with the *trans* configuration, although photoisomerization was not explicitly considered.[12–14,16–21,23–24] The *cis* form might also be less enhanced by resonance RE, thereby possibly escaping observation.

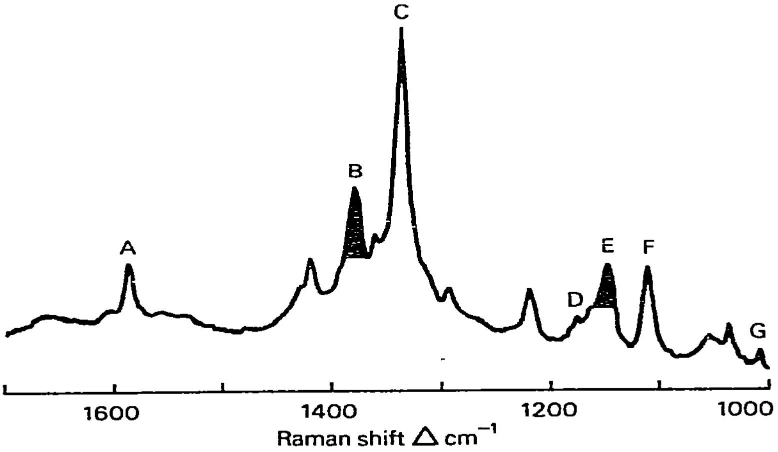


Fig. 5. Raman spectrum of **3** in water (10^{-4} M). $\lambda_{exc.}$ = 514·5 nm.

The second normal mode, ν_2, with the approximate C—N stretch character is assigned to band E near 1140 cm^{-1} in conformity with other authors.[10,12,13,15,16,18–24] Except for **1**(NO$_2$), this appears to be the second also in intensity, as judged qualitatively from the relative preponderance of the Raman lines.

The third mode, ν_3, which represents an in-plane C—N—N—C bending ('Azo-Schlange' vibration[6]) is expected at much lower frequencies. It was tentatively assigned to a vibration at 398 cm^{-1} in azobenzene by Kuebler *et al.*[6] Other authors[12,13,22] opted for a wavenumber range near 1190 cm^{-1}. However, deuteration experiments proved the 1190 cm^{-1} vibration to be a CH in-plane mode.[16] Consequently, band D in the Group II spectra belongs most probably to a CH ring deformation and not to ν_3.

The Raman lines A and G are similarly assigned in both groups, G arising from a ring CH deformation mode.

Concluding this section, the following remarks might be considered appropriate. First, the spectral features of the phenylazonaphthol derivatives **2**(NO$_2$) and **2**(CN) are in accord with the reported hydrazone predominance.[27,28] Secondly, the Raman spectra of phenylazonaphthylamines **1** are in good agreement with a *trans*-azo structure. Thirdly, this agreement indicates that the tautomeric equilibrium is strongly shifted toward the azo form but it does not constitute an irrefutable proof of this shift. Due to resonance RE there is always a remote chance that a minor component in an equilibrium could be enhanced out of all proportion. The spectral features of this might then completely overshadow those of the major component, thereby simulating an inversion of the equilibrium position. Such a case has, in fact, been reported with the involvement of tautomeric structures.[23] This restriction is, however, of little consequence to the present case as NMR measurements and X-ray data[39] also supplement the conclusion arrived at in this section.

4. NMR EVIDENCE

Nuclear magnetic resonance has been applied to azo–hydrazone type equilibria of dyes such as arylazohydroxyaryls,[27,38–42] pyrazolones,[38,41,43–47] 1,3-dicarbonyls[38,48–50] or heterocycles less frequently encountered in commercial use.[46,47] The methods described take advantage of ^{1}H-chemical shift arguments,[38,39,42,44–50] of ^{14}N-chemical shifts measured under double resonance conditions[27] and of the ^{15}N–^{1}H coupling in isotopically labelled dyes.[40,41,43,47,50] The chemical shifts of the labile hydrazonic NH or aromatic OH protons have also been considered in some cases for tautomeric structure discrimination[39,42,46] but at least in the case of 1-phenylazo-2-naphthol derivatives they did not correlate with results from ^{14}N double irradiation experiments.[27] The latter have been demonstrated to be reliable by comparing the results with an independent method, utilizing $J(^{15}N-^{1}H)$.[27,40] The hydrazone content of **2(H)** for instance was estimated by both techniques to be the same within experimental error (79% vs 73·8 ± 5% in $CDCl_3$ at ambient temperature).

From the presently investigated compounds, nearly equal amounts of azo and hydrazone tautomers (48:52) have been found in $CDCl_3$ from $\delta(^{14}N)$ measurements for **2(MeO)** and a strong hydrazone predominance (97%) for **2(CN)**.[27] No results were obtained by this method for **2(NO$_2$)**, due to a broad NH signal which failed to sharpen under ^{14}N-irradiation.[27]

In the case of **2(MeO)** some other reports are at variance with these findings. According to Kaul *et al.* **2(MeO)** 'seems to exist entirely in the azophenol form' in CCl_4 solution as the proton shifts of the *p*-methoxyphenyl moiety are nearly identical to those of 5-methyl-4′-methoxyazobenzene, known to have the azo structure.[38] This method, however, is possibly too crude to assess K_T with any acceptable accuracy, particularly if fast proton exchange between the various sites is involved.

On the other hand, Saeva calculated thermodynamic functions from the temperature dependence of the tautomeric equilibrium constants of two methoxyphenylazonaphthols in acetone–d_6[39] and has received benevolent attention from the reviewing community.[51] Unfortunately, the underlying experiments are questionable and open to criticism. Firstly, for **2(MeO)** one single acidic proton resonance has been found at δ 16·2 ppm which was assigned to the hydroxyl group on assumption of a *slow* proton exchange between the O and N sites. This signal was then integrated with respect to the time averaged *peri* naphthalene proton for the evaluation of K_T.[39] Proton exchange, however, is fast on NMR time scale in phenylazo-2-naphthols[27] and structurally related Schiff bases.[52] Thus, only one signal should appear at an average position and should integrate to unity. Any deviation from unity must be attributed to experimental shortcomings and it is hard to conceive its relationship to K_T. Secondly, for the isomeric 1,4-naphthol derivative two labile proton resonances have been found (δ 10·19 and 3·59) and assigned to NH and OH protons, respectively. Their integrals served to calculate K_T directly. The low field signal might be the time averaged resonance of the proton in rapid exchange between the two sites while the peak at 3·59 must arise from some impurity, probably water. Naphthalenic OH resonance in a hydrogen bonding environment should appear at much lower fields as indicated by the hydroxylic proton shift of 1-naphthol (δ 8·93 ppm) in acetone–d_6.

We consider therefore the results of Berrie *et al.*[27] as the most reliable reported so far for **2(MeO)** and **2(CN)**. They correspond to a K_T of about 1·08 and 32·3 in deuterio-chloroform at ambient temperature.

Our own NMR work comprises ^1H and ^{13}C measurements of dyes **1(R)** and **2(R)** with R = MeO, CN and NO_2 in $CDCl_3$ solutions. The most prominent features of these are illustrated in Fig. 6.

^{13}C-NMR spectra will be discussed first. The tautomers are best differentiated by

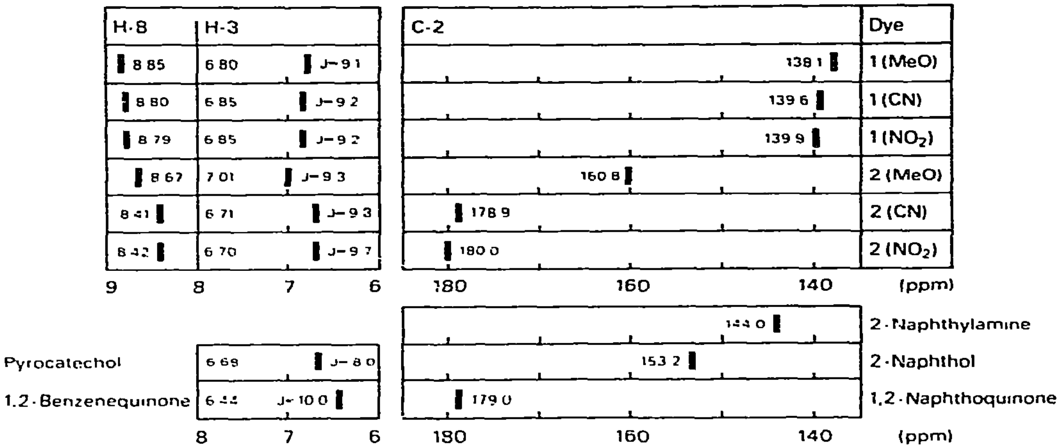


Fig. 6. ^1H and ^{13}C NMR spectral data of the azo dyes (top) and reference compounds (bottom) in $CDCl_3$. *J* refers to coupling between H-3 and H-4 in Hz. Reference values for carbon[53] and proton[55] chemical shifts are taken from the literature.

the chemical shift of C(2). The latter is part of a quinoid structure in the hydrazone and aromatic in the azo form. In Fig. 6 some typical examples of both types are included. Generally, the quinoid carbon absorbs at a lower field as compared to the corresponding aromatic one; this can be seen from the reference compounds[53] (for the chemical shifts of imino carbons, cf. ref. 54). A comparison of the presented data shows that the naphthylamines are predominantly in the azo form whereas the naphthol derivatives with electron withdrawing substituents are far on the hydrazone side. The C(2) chemical shift of **2**(MeO) points to an intermediate equilibrium position. Assuming that **1**(MeO) and **2**(NO_2) represent pure azo and hydrazone tautomers, respectively, K_T of **2**(MeO) can be calculated after correcting for the differing influence of OH and NH_2 substituents on δ-C(2) ($\Delta\delta = 9{\cdot}2$ ppm). The latter is obtained from the chemical shifts of 2-naphthol and 2-naphthylamine. A K_T of 0·7 has thus been estimated. In this calculation, differences in R and in the hydrogen bonding strength of X, which may affect δ-C(2), have been neglected.

The K_T obtained is of the same order of magnitude as the reported value[27] based on δ-(^{14}N) but indicates a somewhat higher azo content in apparently better agreement with UV spectra in chloroform.[28] Unfortunately, an exact evaluation of K_T from UV data is impossible due to strongly overlapping bands.

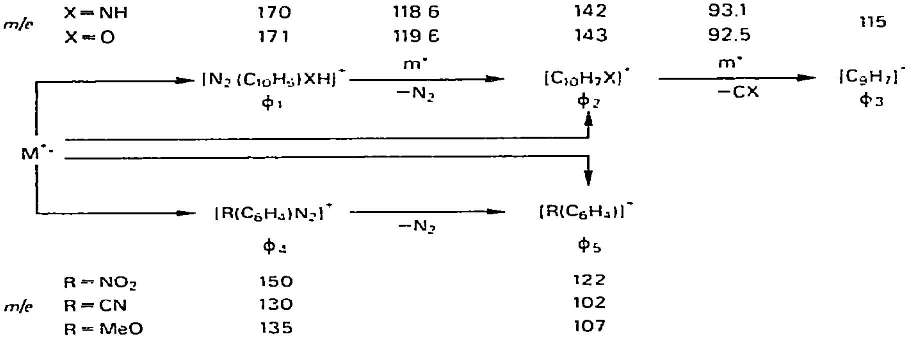
The ^{13}C results are corroborated by ^1H-NMR data. The two tautomers differ in δ-H(3) and *J*(3,4). In quinoid systems H(3) absorbs at a higher field than in phenolic rings and the coupling constant *J*(3,4) becomes larger (cf. Fig. 6). In comparing naphthylamines and naphthols, however, the difference in the NH_2 and OH induced upfield shift of H(3) (0·27 ppm[55]) has to be taken in account. Furthermore, varying *peri* proton (H-8) shifts are observed for the two tautomers due to different substituents on C(1). This shift can also be used for the calculation of K_T for **2(MeO)**. A value of 0·7 is obtained again.

The NMR data thus support the conclusion that the phenylazonaphthylamines under investigation are best described as azo tautomers, in complete agreement with deductions arrived in Part I[2] and in the preceding section.

5. MASS SPECTRA

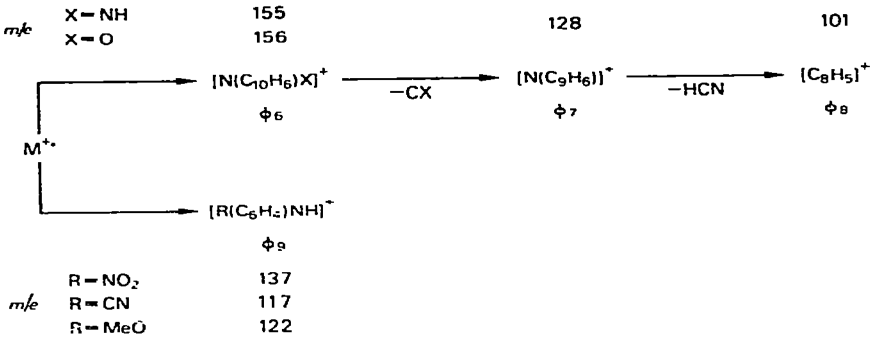
Recently, Kostyuchenko *et al.* reported that the molecular ion of tautomeric monoazo dyes cleaves preferentially at the NN bond in the hydrazone and at one of the CN bonds in the azo tautomer, yielding high abundance fragments with corresponding metastable ions.[56] These results suggested the utility of mass spectrometric methods for azo–hydrazone type structure discrimination and therefore the mass spectra of **1(R)** and **2(R)** with R = MeO, CN and NO_2 have been included in our investigation.

With these dyes the main decomposition route originates from a primary CN cleavage (Scheme 2) irrespective of the tautomeric structure found for them in solution or in the crystalline state.[33]



Scheme 2. Decomposition pathway following primary CN cleavage.

A good example is provided by the spectra of **1(NO_2)** and **2(NO_2)** in Fig. 7. The few prominent ions have either the same mass-to-charge ratio in both spectra (ϕ_3) or differ by one *m/e* unit ($M^{+\cdot}$, ϕ_1 and ϕ_2) due to the difference in the mass of NH and O. High abundance peaks in all cases studied have been found for $M^{+\cdot}$, ϕ_2 and ϕ_3 (Table 3) with metastables showing a $\phi_1 \rightarrow \phi_2$ and a $\phi_2 \rightarrow \phi_3$ transition. The low intensity of the ions ϕ_6–ϕ_9 speaks against a major decomposition pathway with initial NN cleavage (Scheme 3). It has to be pointed out that the NN cleavage route provides a noteworthy contribution to the total ion current only in the case of **2(MeO)** but here too, products of the CN bond cleavage predominate.



Scheme 3. Decomposition pathway following primary NN cleavage.

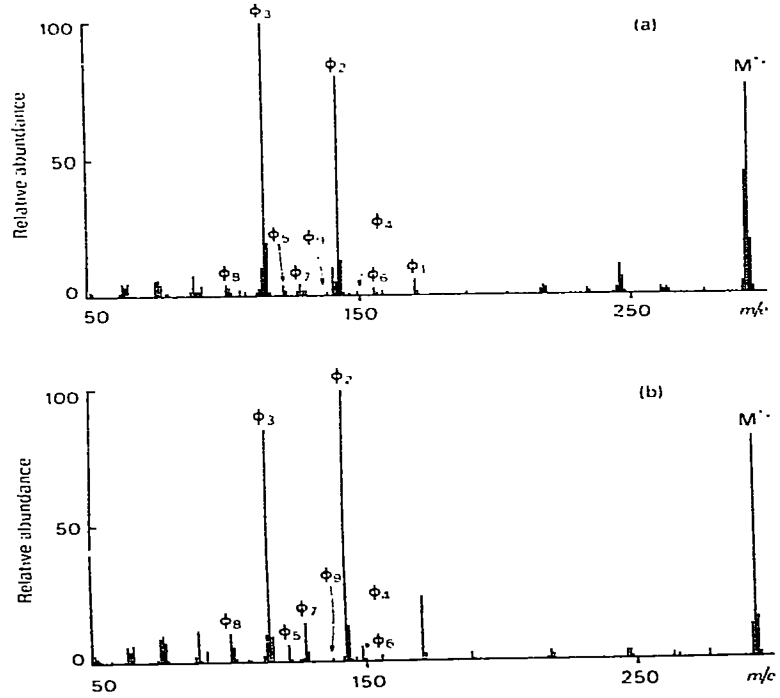


Fig. 7. Mass spectra of (a) $1(NO_2)$ and (b) $2(NO_2)$ at 130 and 140 °C, respectively.

TABLE 3

RELATIVE ABUNDANCE (%) OF MOLECULAR AND FRAGMENT IONS[a]

		Primary C—N cleavage					Primary N—N cleavage			
	$M^{+\cdot}$	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8	ϕ_9
1(NO_2)	76·7	6·1	80·6	100·0	—	3·8	—	4·2	4·0	—
1(CN)	63·7	4·9	86·1	100·0	—	15·4	—	3·9	4·2	3·8
1(MeO)	100·0	4·4	71·3	69·1	4·7	32·4	3·6	3·6	3·5	3·2
2(NO_2)	81·6	23·8	100·0	85·6	—	6·5	—	14·7	10·8	—
2(CN)	71·0	23·1	100·0	71·5	—	18·9	—	9·3	11·6	—
2(MeO)	100·0	10·9	56·0	42·5	19·8	54·9	6·4	14·2	8·0	12·7

[a] Low resolution spectra, ionization potential 70 eV, temperature range 90–140 °C. The elemental composition of the ions was determined by high resolution measurement.

These results are in apparent contradiction to all observations we have reported so far and cannot be explained satisfactorily by a general displacement of the tautomeric equilibria originating from the evaporation or ionization process in the mass spectrometer. By an increase of K_T upon ionization a predominant NN cleavage of $M^{+\cdot}$ should be expected at least with the naphthol dyes **2** and in the case of a decrease of K_T a CN fragmentation should be preponderant, eventually with an additional NN decomposition route for **2**(NO_2) instead of **2**(MeO).

The following argument will prove that the present observation can be reconciled with the results obtained by other methods without the necessity of assuming a substantial equilibrium shift under mass spectrometric conditions.

We shall assume that the weakest bond in $M^{+\cdot}$ will determine the primary cleavage route and vibronic excitation does not need to be dealt with explicitly. Let us consider pure single and double bonds formed by a pair of sp^2 hybridized atoms. Their bond energies are shown as functions of the bond length for NN, CN, CC and CO atomic pairs in Fig. 8. The plot was prepared from data published by Dewar and Morita.[57] The difference between the corresponding single and double bond curves is just the π-bonding energy, $E_{\pi b}$, and any actual bond will lie on some path joining the encircled vertices, within the area enclosed by these curves and the vertical lines drawn at the equilibrium bond length.

If the π-bonding contribution to each bond type is the same, the NN bond will be the weakest and the CO bond the strongest with CN and CC bonds being intermediate. Assuming equal vibrational excitation, the NN and CN bonds should therefore cleave preferentially. In order to obtain a primary CN cleavage, however, $E_{\pi b}$ (and with it the π-bond order) of the NN bond must be considerably higher than that of the CN bond.

This condition is generally fulfilled for the azo structures in their ionized state as follows from the mass spectrometric behaviour reported for non-tautomeric azo dyes.[58] HMO bond orders calculated for the molecular ion of the azo tautomer of **2** are in good qualitative agreement with this requirement irrespective of the nature of

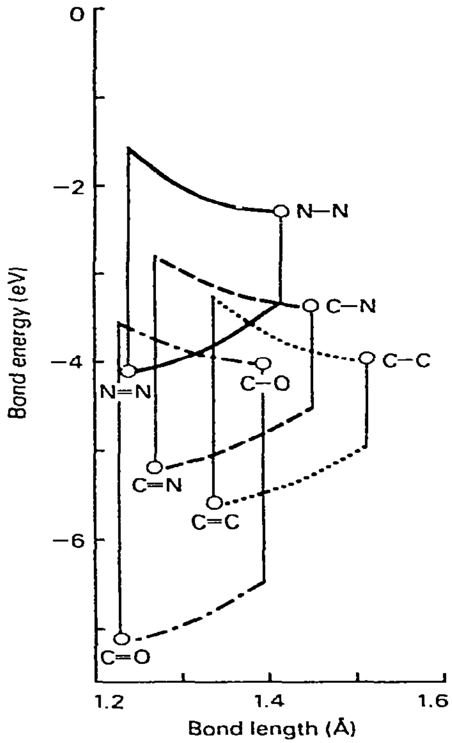


Fig. 8. Potential energy (Morse) curves in the bond length range of single and double bonds formed by sp^2 hybridized atoms plotted from bond dissociation energies and Morse constants reported by Dewar and Morita.[57] The origin of the energy scale corresponds to the bond dissociation limit.

the substituent R (Fig. 9a). The substituent effects were taken into account by an inductive model described in Part I using the same parameters.[2]

Turning to the hydrazones, Fig. 9b indicates that with electron acceptor substituents the order of the CN bond in $M^{+\cdot}$ is considerably lower than that of the NN bond. This agrees with the preferred CN cleavage in the case of 2(CN) and 2(NO_2). A similar explanation holds true for derivatives of 2-(4′,6′-disubstituted-2′-*s*-triazinylazo)-1-naphthol which cleave exclusively at the CN bond in the primary step although they are known to exist as hydrazones prior to electron impact.[59]

On the other hand, with increasing electron donor strength of R the difference between the order of the CN and NN bonds becomes progressively less significant and competition between both primary bond cleavages might occur. This is precisely what is observed for 2(MeO).

Once the decomposition of the hydrazone is initiated by breaking the CN bond, the emerging cation $[HN{-}N{=}(C_{10}H_6){=}X]^+$ rearranges to the more stable ϕ_1 and

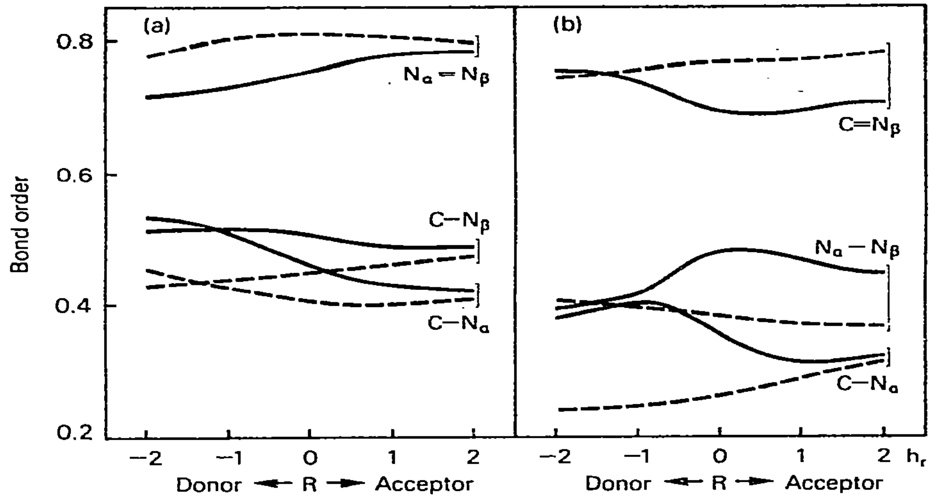


Fig. 9. Substituent dependency of HMO bond orders for (a) the azo and (b) the hydrazone forms of 2 (dashed curves) and their molecular ions (solid curves). The effect of R is taken into account by the perturbation (h_r) it exerts on the Coulomb integral of the substituent-bearing carbon atom.

the further fragmentation steps are of the same type for both azo and hydrazone tautomers, thus explaining the great similarity of the spectra of widely differing structures.

Although the mass spectra do not confirm the tautomeric structure of the investigated dyes the presented arguments show that the results are not in contradiction to those obtained by other methods.

ADDENDUM

After submission of this paper two studies have appeared on the same general subject utilizing other ^{13}C- and ^{15}N-NMR chemical shift arguments for the estimation of K_T of isotopically labelled tautomeric azo dyes (A. Lyčka, D. Šnobl, V. Macháček and M. Večeřa, *Org. Magn. Resonance*, **15**, 390 (1981); **16**, 17 (1981)). No direct comparison with our results is, however, possible as the studied compounds are not identical.

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