STUDY OF THE AZO–HYDRAZONE TAUTOMERIC EQUILIBRIUM BY ELECTRONIC SPECTROSCOPY AND QUANTUM CHEMISTRY. I. ELECTRONIC SPECTRA

Miloš Nepraš, Miloš Titz, Miroslav Nečas, Stanislav Luňák jr,
Radim Hrdina and Antonín Lyčka

Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví

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Dedicated to Prof. Jaromír Horák on the occasion of his 60th birthday.

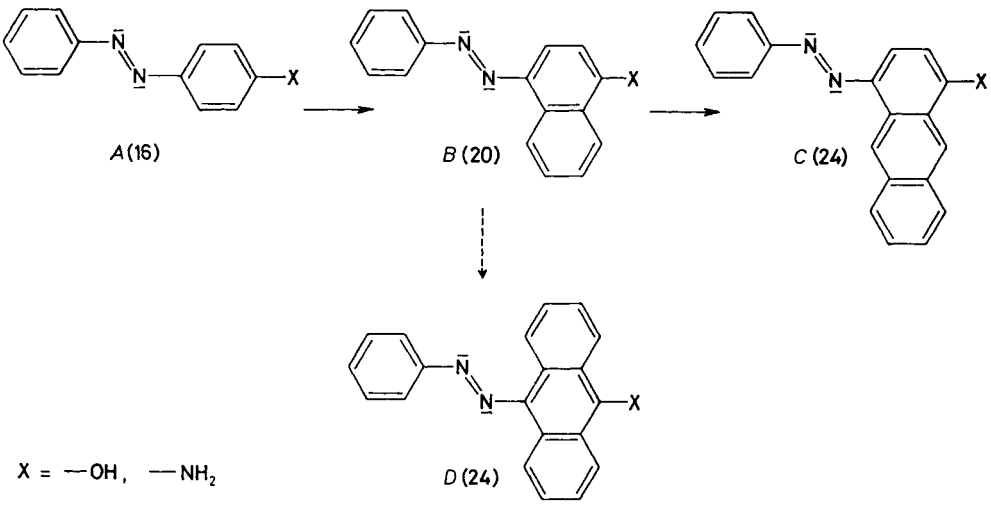
The azo–hydrazone tautomeric equilibrium was studied for *p*-hydroxy and *p*-amino derivatives of some arylazo compounds. Substantial differences were observed between the spectral patterns in hydrocarbon and alcoholic solutions at normal and low temperatures; these are due to shifts in the azo–hydrazone tautomeric equilibrium, which depends on the nature of the proton donor *para* substituent, size and topology of the system (aromatic ring fusion patterns), solvent and temperature. The spectral patterns suggest that the proton transfer from the para substituent takes place after dimerization of the molecule.

Azo dyes offer the widest choice of synthetic dyes in shades covering the entire visible spectral region. Many azo compounds possessing a proton donor substituent in a suitable position can exist in the azo–hydrazone tautomeric equilibrium. From the colorist point of view this is an unwanted effect bringing about change in the dye shade and its stability (photochemical stability in particular).

Although azo–hydrazone tautomerism is receiving considerable interest (refs[1-4] and references therein), a number of problems still exist concerning the relation between the molecular and electronic structure of the compounds and the proton tranfer mechanism. It should be noted that the individual experimental techniques only offer a more or less single-tracked view upon this topic; so one has to be circumspect enough not to generalize the results of some of them too much or even to regard some of the methods as universal.

In this paper we report on the results of experimental investigation of the relation between the molecular and electronic structure of *p*-hydroxy and *p*-aminoderivatives of some arylazo compounds and the proton transfer mechanism. Their azo–hydrazone tautomeric equilibrium is examined by UV-VIS spectrophotometry in dependence on the nature of solvent and on temperature (from 20°C down to −170°C); their fluorescence behaviour is also studied under these conditions.

The azo–hydrazone tautomeric equilibrium is known[1-4] to be affected considerably by the nature and position of the proton donor substituent, medium and temperature, and also by the aromatic ring fusion patterns, hence, the size and topology of the system. In this work, pairs of mutually isoelectronic *p*-hydroxy and *p*-amino derivatives of systems *A* through *D* in Scheme 1 are studied (in Scheme 1, the numbers



SCHEME 1

of π-electrons, *n*, of the *para* substituted system are given in parentheses). In this scheme, four *para* substituted azo systems (*A*(X) through *D*(X)) are shown, the arrows between them indicating the benzene ring fusion at the part of the hydrocarbon fragment where the hydroxy or amino group occurs in the *para* position to the azo group (e.g., *A*(X) system → *B*(X) system ⇢ *D*(X) system). The *A*(X), *B*(X), and *C*(X) systems form a ring fusion series and can be referred to as 1,4-systems, whereas the *D*(X) system can be referred to as a 9,10-system, constituting the first member in a different ring fusion series; *B*(X) ⇢ *D*(X) thus is a transition from the series of 1,4-systems to 9,10-systems.

EXPERIMENTAL

The compounds used were synthesized conventionally and purified by column chromatography on Al_2O_3 and crystallization. Solvents were purified conventionally to attain spectral purity.

Electronic absorption spectra were measured on a Perkin–Elmer 555 spectrophotometer; a homebuilt adapter was used for low-temperature measurements. The solution temperature was measured with a resistance thermocouple submerged in the cell. All the spectra shown are corrected for temperature changes of solution volume.

Luminescence spectra were measured on a Perkin–Elmer LS-5 spectrofluorimeter equipped with an accessory for measurements at liquid nitrogen temperature. The excitation spectra are corrected whereas the fluorescence spectra are not.

RESULTS

Fig. 1 shows the absorption curves of 1-phenylazo-4-naphthol in a methylcyclohexane–3-methylpentane 5 : 2 mixture (henceforth referred to as the hydrocarbon solvent) at 20°C and −170°C. In accordance with the results of Fischer and Frei[5], in this solvent the azo–hydrazone equilibrium is shifted towards the latter at low temperatures. The absorption curve in Fig. 1 measured at a low temperature is regarded as corresponding to the hydrazone form. Aromatic azo compounds are known to exhibit no fluorescence even at low temperatures. Where fluorescence was observed, it was attributed to the hydrazone form[6]. The compound studied displays very weak fluorescence with a maximum at $1{\cdot}87 \cdot 10^4\ cm^{-1}$ in ethanol and chloroform at room temperature; at a low temperature in the hydrocarbon solvent the fluorescence is relatively more intense and its maximum lies at $1{\cdot}85 \cdot 10^4\ cm^{-1}$ (Fig. 1).

The identical patterns of the fluorescence excitation spectrum and the absorption curve in the hydrocarbon solvent at a low temperature (Fig. 1) give evidence that under these conditions, 1-phenylazo-4-naphthol exists in the hydrazone form solely.

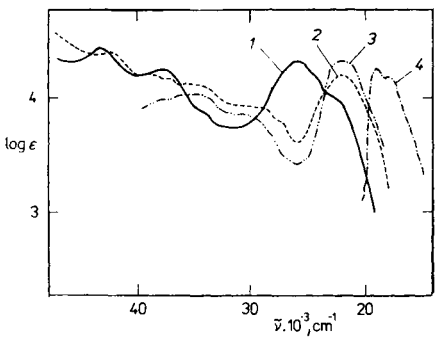


FIG. 1

Electronic spectra of 1-phenylazo-4-naphthol in hydrocarbon solvent (methylcyclohexane + 3-methylpentane 5 : 2). *1* Absorption spectrum at 20°C, *2* absorption spectrum at −170°C, *3* fluorescence excitation spectrum in the fluorescence band maximum at −196°C, *4* fluorescence spectrum at −196°C

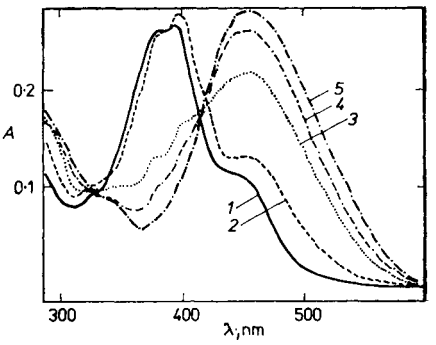


FIG. 2

Absorption spectra of 1-phenylazo-4-naphthol in methylcyclohexane. Temperature (°C): *1* 20, *2* −3, *3* −16, *4* −23, *5* −30

Absorption curves of this compound in methylcyclohexane at temperatures from 20°C down to −30°C are shown in Fig. 2. Cooling this solution to −3°C brings about a more pronounced vibronic structure of the band in the 380 nm range, belonging to the azo form, and intensity increase of the band of the hydrazone form at 450–550 nm. At −16°C, the two forms coexist in the solution, the equilibrium being shifted in favour of the hydrazone form. Additional temperature decrease is accompanied by an additional shift of the equilibrium in favour of the hydrazone form, which predominates highly at −30°C. The system of absorption curves gives rise to a clear-cut isosbestic point, giving evidence that a simple azo ⇄ hydrazone equilibrium establishes in this solvent. The corresponding equilibrium constants were determined at different temperatures and the values

$$\Delta H = -24{\cdot}1 \text{ MJ mol}^{-1}, \quad \Delta G^0_{293} = 2{\cdot}9 \text{ MJ mol}^{-1}, \quad \Delta S^0_{293} = -92{\cdot}2 \text{ kJ K}^{-1}$$

were calculated from them. The temperature dependence of absorbance of the hydrazone form at 460 nm has a typical sigmoid shape (Fig. 3), giving evidence of the occurrence of the equilibrium. In the hydrocarbon solvent at −60°C, 1-phenylazo-4-naphthol occurs in the hydrazone form. The plot of ln K vs $1/T$, which served to calculate the ΔH value, is shown in Fig. 4. The value of $K = 1$ is attained at −14°C (inflection range of the sigmoid curve). For a comparison, values derived from NMR data[7] are also included in this plot; it is clear that this dependence is steeper than the dependence for our values derived from electronic spectral data.

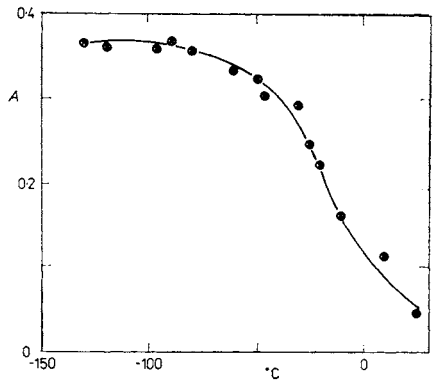


FIG. 3

Dependence of absorbance on temperature for 1-phenylazo-4-naphthol in the range of absorption by its hydrazone form (460 nm)

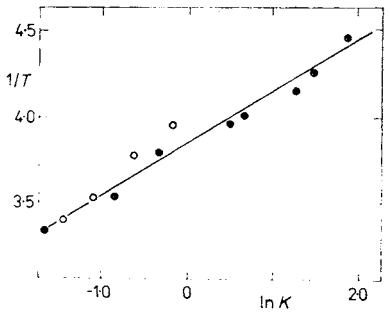


FIG. 4

Plot of ln K vs $1/T$ for 1-phenylazo-4-naphthol in hydrocarbon solvent. ● Our data derived from absorption measurements, ○ data derived from NMR measurements[7]

Despite the different solvents used (the NMR measurements were performed with acetone solutions at concentrations higher by an order of magnitude), the thermodynamic values obtained by us agree very well with those obtained from NMR data ($\Delta H = -18{\cdot}8$ MJ mol^{-1}, $\Delta G^0_{293} = 3{\cdot}4$ MJ mol^{-1}, $\Delta S^0_{293} = -75{\cdot}8$ kJ K^{-1}).

Fig. 5 shows the absorption curves of 1-phenylazo-4-naphthol in ethanol at 20°C and −170°C. The spectra give evidence that in contrast to the hydrocarbon solvent, in ethanol the equilibrium shifts in favour of the azo form with decreasing temperature; the absorption in the region of the $\pi\pi^*$ band of the azo form increases at the expense of that in the hydrazone band region.

For a comparison, Fig. 6 shows the electronic absorption spectrum of 1-phenylazo-4-methoxynaphthalene, hence, a substance that cannot exist in the hydrazone form. As expected, only a better developed vibronic structure of the first $\pi\pi^*$ absorption band appears on temperature lowering (the shoulder in the $2{\cdot}20 \cdot 10^4$ cm^{-1} region corresponds to the $\pi^* \leftarrow n$ transition).

Fig. 7 shows the electronic absorption spectra of 1-phenylazo-4-aminonaphthalene in ethanol at 20°C and −170°C. The first absorption band becomes narrower and its intensity in the band maximum increases on temperature lowering, but no formation of the hydrazone form is observed.

Fig. 8 shows the electronic absorption spectra of 1-phenylazo-4-aminonaphthalene in the hydrocarbon solvent at 20°C and −170°C; absorption curves for some temperatures within this region are plotted in Fig. 9. The spectra are clearly different from those in ethanolic solution. Temperature lowering to approximately −35°C (curve 2) only brings about a slight bathochromic shift of the absorption band of the azo form, which gets narrower and more intense in the maximum. If the tempera-

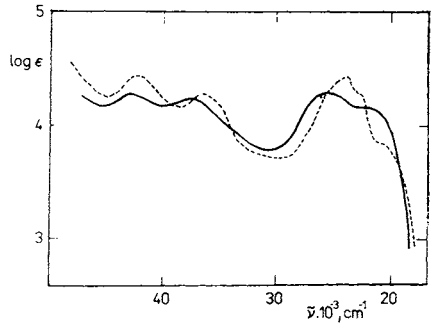


FIG. 5

Absorption spectra of 1-phenylazo-4-naphthol in ethanol at 20°C (———) and −170°C (– – – –)

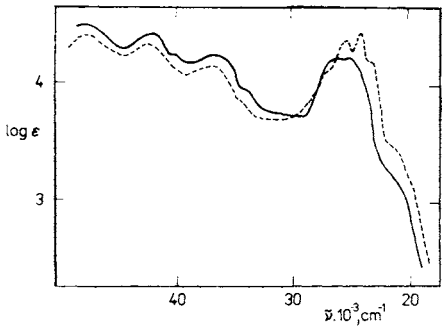


FIG. 6

Absorption spectra of 1-phenylazo-4-methoxynaphthalene in hydrocarbon solvent at 20°C (———) and −170°C (– – – –)

ture is further lowered, however, two new absorption bands appear at 450 nm and 480–500 nm; the ratio of their heights changes in favour of the latter on additional temperature lowering (curves *3* and *4* in Fig. 9); the intensity of the band at 410 to 430 nm decreases. Further temperature decrease does not affect the spectral patterns appreciably (curves *5* and *6*). The absorption curves shown in Fig. 9 indicate that for 1-phenylazo-4-aminonaphthalene, some phenomena different from a simple

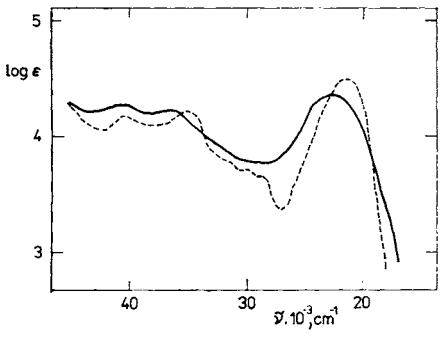


FIG. 7

Absorption spectra of 1-phenylazo-4-aminonaphthalene in ethanol at 20°C (———) and −170°C (– – – –)

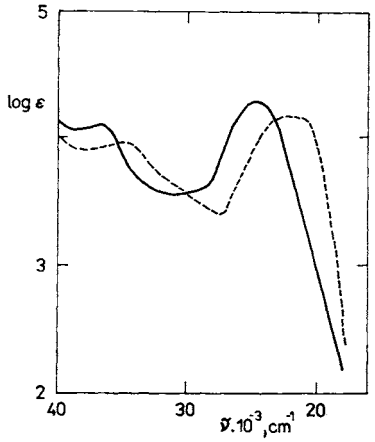


FIG. 8

Absorption spectra of 1-phenylazo-4-aminonaphthalene in hydrocarbon solvent at 20°C (———) and −170°C (– – – –)

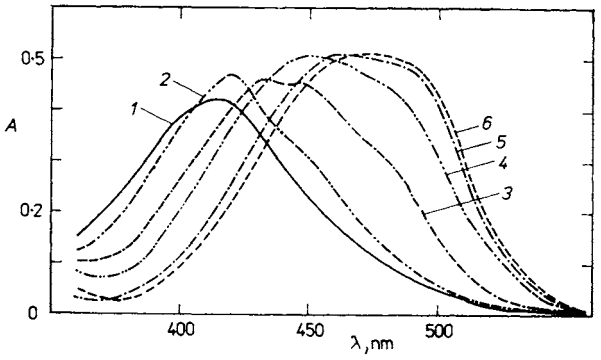


FIG. 9

Absorption spectra of 1-phenylazo-4-aminoaphthalene in hydrocarbon solvent. Temperature (°C): *1* 20, *2* −35, *3* −65, *4* −120, *5* −140, *6* −170

azo–hydrazone equilibrium are involved. No luminescence of this compound in the hydrocarbon solvent was observed even at −196°C. The temperature dependence of absorbance of this compound at 490 nm, both in the hydrocarbon solvent and in ethanol, is shown in Fig. 10. The sigmoid shape of this dependence in the former solvent points to the occurrence of an equilibrium in the system; the linear shape of this dependence in the latter solvent, on the other hand, gives evidence that only changes associated with a peak shift and changes in the shape of the absorption band of the azo form take place. Similar linear dependences were obtained in both solvents for the *p*-methoxy and *p*-(N,N-dimethylamino) derivatives, hence, compounds existing in the azo form solely. The absorption spectra of 1-phenylazo-4-(N,N-dimethylamino)naphthalene in the two solvents at 20°C and −170°C are shown in Figs 11 and 12. This compound cannot exist in the hydrazone form and so, as expected, the spectral patterns in the two solvents and at the two temperatures are identical, corresponding to the azo form.

Fig. 13 shows the electronic absorption spectra of 4-hydroxyazobenzene in ethanol at room temperature and at −170°C. The spectral patterns are virtually temperature independent. This compound exists in ethanol in the azo form solely at these temperatures. In the hydrocarbon solvent, on the other hand, the spectral patterns alter with temperature (Figs 14 and 15). On cooling the solution to −80°C (Fig. 15, curve

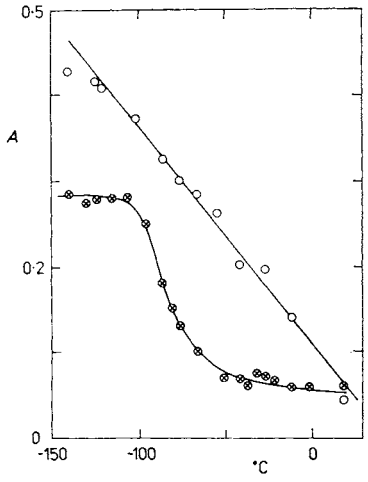


FIG. 10

Dependence of absorbance of 1-phenylazo-4-aminonaphthalene at 490 nm on temperature. ⊗ Hydrocarbon solvent, ○ ethanol

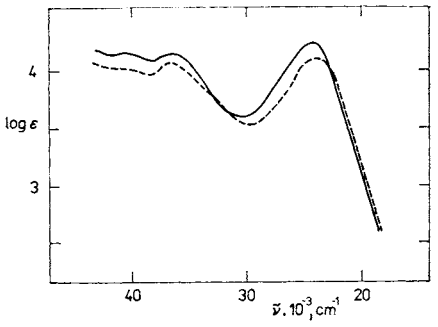


FIG. 11

Absorption spectra of 1-phenylazo-4-(N,N-dimethylamino)naphthalene in hydrocarbon solvent at 20°C (———) and −170°C (– – – –)

2), the absorbance in the $\pi\pi^*$ band region decreases whereas that in the 370 nm range increases. This trend continues at −145°C (curve 3), a band at 370 nm and another at 400–460 nm starting to separate. At −170°C (curve 4), the band at 370 nm is completely separated and the new band at 400–460 nm is clearly apparent; obviously, the spectra at −80°C and −145°C are superpositions of those of the azo form and a new species whose absorption maximum lies at 370 nm. Unlike Rau[6], we observed no fluorescence even at −196°C. For a comparison, Figs 16 and 17 show the absorption spectra of 4-methoxyazobenzene in the two solvents

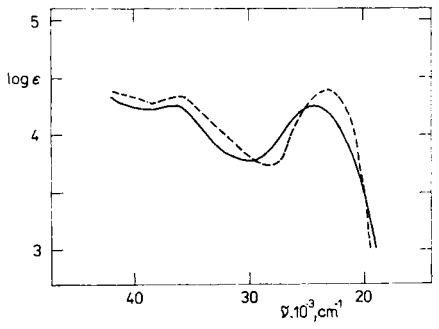


FIG. 12

Absorption spectra of 1-phenylazo-4-(N,N-dimethylamino)naphthalene in ethanol at 20°C (———) and −170°C (- - - - -)

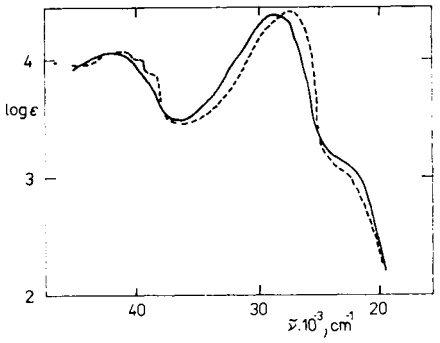


FIG. 13

Absorption spectra of 4-hydroxyazobenzene in ethanol at 20°C (———) and −170°C (- - - - -)

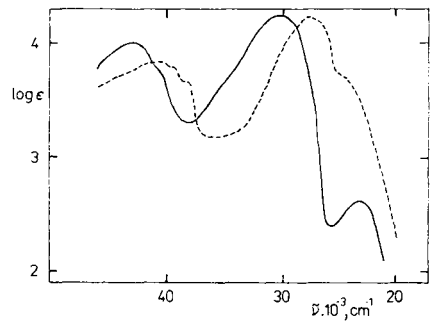


FIG. 14

Absorption spectra of 4-hydroxyazobenzene in hydrocarbon solvent at 20°C (———) and −170°C (- - - - -)

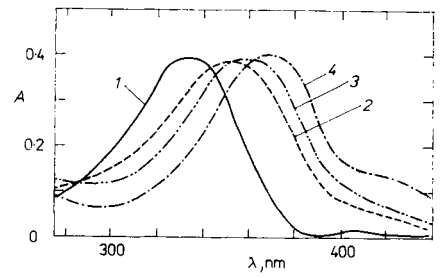


FIG. 15

Absorption spectra of 4-hydroxyazobenzene in hydrocarbon solvent. Temperature (°C): *1* 20, *2* −80, *3* −145, *4* −170

at 20°C and −170°C. As expected, the spectral patterns are identical in all cases, corresponding to the azo form of the compound.

Fig. 18 shows the electronic absorption spectra of 4-aminoazobenzene in ethanol at 20°C and −170°C. The temperature decrease is only associated with a slight bathochromic shift of the first intense $\pi\pi^*$ absorption band and increase in its intensity accompanied by its narrowing. It is clear that under these conditions, the compound exists in the azo form solely.

In the hydrocarbon solvent, the spectra of 4-aminoazobenzene are different (Figs 19 and 20). Cooled to −85°C, the solution exhibits a bathochromic shift of

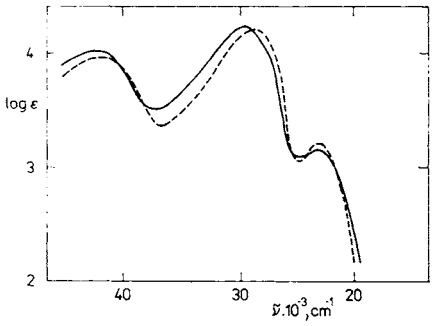


FIG. 16

Absorption spectra of 4-methoxyazobenzene in ethanol at 20°C (———) and −170°C (- - - - -)

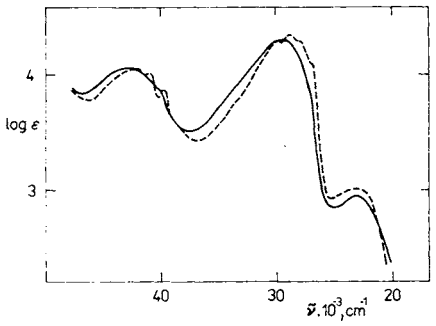


FIG. 17

Absorption spectra of 4-methoxyazobenzene in hydrocarbon solvent at 20°C (———) and −170°C (- - - - -)

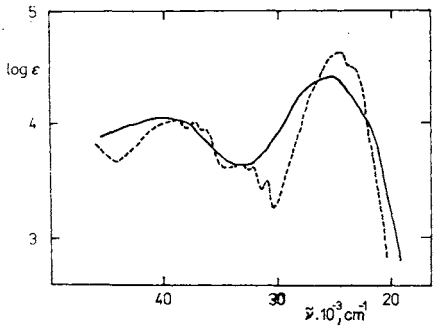


FIG. 18

Absorption spectra of 4-aminoazobenzene in ethanol at 20°C (———) and −170°C (- - - - -)

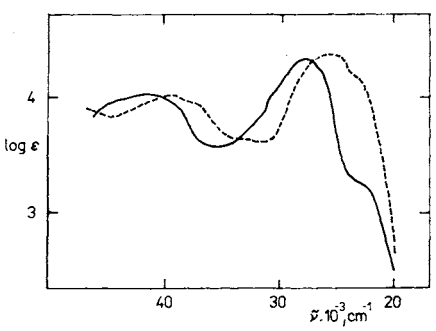


FIG. 19

Absorption spectra of 4-aminoazobenzene in hydrocarbon solvent at 20°C (———) and −170°C (- - - - -)

the first intense $\pi\pi^*$ band belonging to the azo form. Additional cooling to −120°C (curve *3*) is accompanied by intensity decrease of this band combined with a slight absorbance increase in the 430 nm range. The spectral patterns are altered at −145°C (curve *4*): the long-wavelength part of the spectrum is seen to comprise an intense band with the maximum at 385 nm and an overlapped band appearing as a shoulder in the 430 nm range. Additional temperature lowering does not affect the spectrum appreciably (curve *5*). Clearly, 4-aminoazobenzene in the hydrocarbon solvent exists in its azo form solely down to a temperature of approximately −100°C. A new equilibrium appears on additional temperature lowering; its establishment is complete at −145°C and is not affected considerably by further cooling. The equilibrium is not a simple azo–hydazone equilibrium such as occurs, e.g., with 1-phenylazo-4-

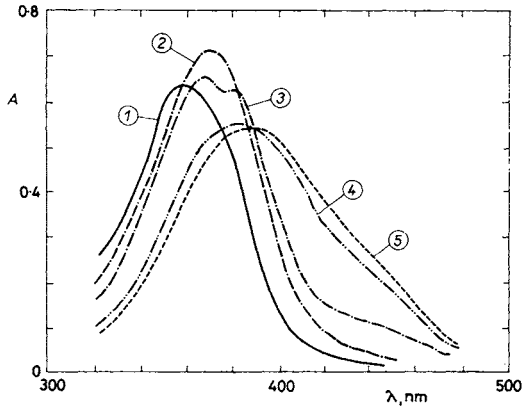


FIG. 20

Absorption spectra of 4-aminoazobenzene in hydrocarbon solvent. Temperature (°C): *1* 20, *2* −85, *3* −120, *4* −145, *5* −170

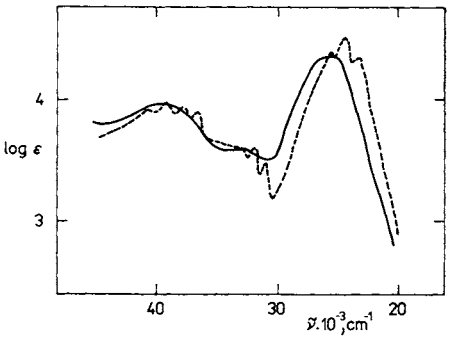


FIG. 21

Absorption spectra of 4-(N,N-dimethylamino)azobenzene in hydrocarbon solvent at 20°C (———) and −170°C (- - - -)

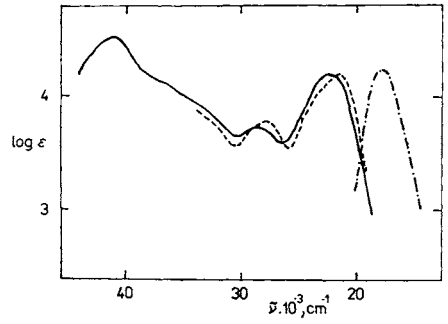


FIG. 22

Electronic spectra of 9-phenylazo-10-hydroxyanthracene in ethanol. ——— absorption spectrum at 20°C, -·-·-·- fluorescence spectrum at 20°C, $\tilde{\nu}_{exc} = 2{\cdot}22 \cdot 10^4\ cm^{-1}$, - - - - - fluorescence excitation spectrum at −196°C, $\tilde{\nu}_{em} = 1{\cdot}83 \cdot 10^4\ cm^{-1}$

-naphthol. 4-Aminoazobenzene in the hydrocarbon solvent exhibits no fluorescence even at liquid nitrogen temperature.

For a comparison, the spectrum of 4-(N,N-dimethylamino)azobenzene in the hydrocarbon solvent and at −170°C is shown in Fig. 21. As expected, only a slight bathochromic shift and a better developed vibronic structure appear on cooling.

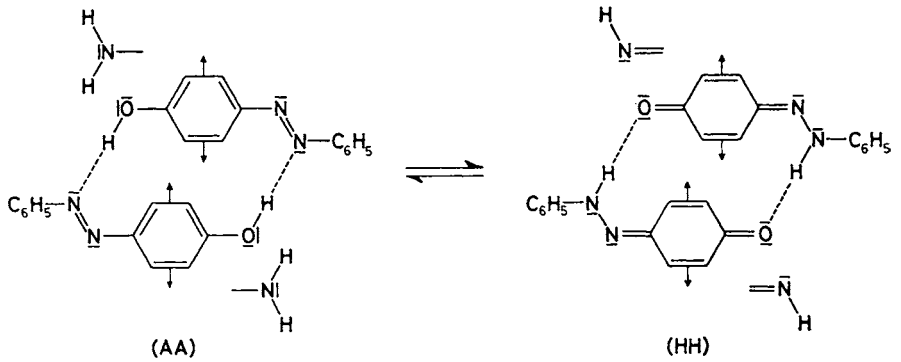
Fig. 22 shows the electronic absorption and fluorescence spectra at 20°C and the fluorescence excitation spectrum at −196°C for 9-phenylazo-10-hydroxyanthracene in ethanol. The identical patterns of the absorption and excitation spectra give evidence that the compound in ethanol exists in the hydrazone form solely even at room temperature; this result is consistent with that obtained by NMR spectrometry[8]. The compound is very low soluble in the hydrocarbon solvent and crystallizes from the solution at low temperatures.

DISCUSSION

Since in hydrocarbon solvents, no solvation of solutes by hydrogen bonding takes place, we suggest that a system of equilibria

$$A + A \overset{K_1}{\rightleftharpoons} (AA) \overset{K_2}{\rightleftharpoons} (HH) \overset{K_3}{\rightleftharpoons} H + H \qquad (A)$$

establishes in them for the compounds studied (A and (AA) are the monomer and dimer of the azo form, respectively, and H and (HH) are the monomer and dimer of the hydrazone form, respectively), hence, the proton transfer from the proton donor *para* substituent to the α-nitrogen atom of the azo group proceeds via intermolecular hydrogen bonds in the dimers (Scheme 2).



SCHEME 2

In solvents that are unable to form hydrogen bonds (hydrocarbons, chloroform, etc.), the spectra indicate that 1-phenylazo-4-naphthol exists in equilibrium with

its hydrazone form even at room temperature. The identical patterns of the absorption spectrum of this compound in the hydrocarbon solvent at −170°C and its excitation spectrum at −196°C (Fig. 1) give evidence that in the hydrocarbon solvent the compound is present in its hydrazone form solely at low temperatures, and predominantly even at −30°C (Figs 2 and 3) (ref.[9]). Within the region of solubility of this substance in the hydrocarbon solvent (up to approximately 0·2 mmol l^{-1}), no spectral evidence of azo form dimerization was obtained at normal or low temperatures. Since only the azo and hydrazone forms are observed (Fig. 2), it is evident that $K_2 \gg K_1$ and the spectrophotometrically established equilibrium constant of the azo–hydrazone equilibrium corresponds to the K_1K_2 product. Thus the rate--determining step in the formation of the hydrazone form is the formation of the azo form dimer. The results do not reveal unambiguously whether the "hydrazone" absorption band in the 455 nm ($2{\cdot}2 \cdot 10^4$ cm^{-1}) region corresponds to the dimer or monomer of the hydrazone form; so we lack any information concerning the magnitude of the equilibrium constant K_3. It is, however, reasonable to assume that in the hydrocarbon solvent the hydrazone form of 1-phenylazo-4-naphthol exists as the dimer only[10]; this is also borne out by the calculation performed for the simple dimer model by the HMO method (see Part II in this issue).

The situation is different with 4-hydroxyazobenzene. In contrast to 1-phenylazo-4--naphthol, the absorption curves of this compound at different temperatures do not form a clear-cut isosbestic point. As the temperature of the solution in the hydrocarbon solvent is lowered, a stage of an aggregated azo form species (presumably the (AA) dimer) is observed; it gives probably rise to an absorption band in the 370 nm range, which develops at the expense of the band at 330 nm belonging to the azo form monomer (Fig. 15). Analogous results have been obtained by Gabor and coworkers[11] who, however, attributed the spectrum at approximately −120°C to the dimer solely. We suppose that at this temperature the nonaggregated azo form is also present to some extent and that the absorption band at 400−460 nm, observed at −170°C only, is due to the hydrazone form. Thus, it can be concluded that in the hydrocarbon solvent, three 4-hydroxyazobenzene species coexist in equilibrium: the azo form, its dimer, and the hydrazone form (dimer or monomer). The equilibrium constants K_1 and K_2 are then commensurable in magnitude. The temperature changes of the absorption curves of 4-aminoazobenzene (Fig. 20) can be interpreted likewise; again, the azo form, its dimer and the dimer or monomer of the hydrazone form seem to coexist in the hydrocarbon solvent at low temperatures.

The temperature dependence of the absorption curves is somewhat different for 1-phenylazo-4-aminonaphthalene, while for the two previous compounds the dimer of the azo form predominated at low temperatures (Figs 15 and 20), for 1-phenylazo--4-aminonaphthalene the concentrations of the azo form dimer and the hydrazone form dimer seem to be comparable (although we lack information about their absorptivities), and a very broad absorption band emerges (Fig. 9). Absorption

curves *4–6* in Fig. 9 show a decrease in absorbance of the azo form dimer at 430 nm and an increase in aborbance of the hydrazone form (monomer or dimer) in a region above 470 nm.

Unlike Rau[6], we observed no fluorescence for 4-hydroxyazobenzene, presumably because of a relatively too low concentration of the hydrazone form in the system; moreover, this species can be expected to have a considerably lower fluorescence quantum yield as compared to the hydrazone form of 1-phenylazo-4-naphthol.

It is also noteworthy that the fluorescence of 4-hydroxyazobenzene at 667 nm observed by Rau exhibits an unlikely high Stokes shift with respect to the fluorescence maximum of the naphthalene analogue, which lies at 550 nm. For the studied amino derivatives in the hydrocarbon solvent, we observed no fluorescence even at −196°C either, presumably because of very low fluorescence quantum yields of their hydrazone forms, the concentration of the hydrazone form of 1-phenylazo-4-aminonaphthalene being certainly high enough.

Alcohols and polar aprotic solvents, whose basic centres are usually constituted by nonbonding electron pairs or π molecular orbitals, can form intermolecular hydrogen bonds with hydrogen atoms of the —OH or $—NH_2$ groups in the *p*-substituted azo compound. The possibility of proton transfer from the *para* substituent to the α-nitrogen atom of the group then is limited, whereby the azo form is stabilized. The azo–hydrazone ratio thus depends to some extent on the acceptor strength of the solvent used. An exception is 9-phenylazo-10-hydroxyanthracene, which occurs in the hydrazone form solely[12]. According to refs[12,13], condensation products of the benzenediazonium ion with anthrols exist nearly solely in the quinonehydrazone form.

In alcoholic solutions, the intermolecular hydrogen bonding between the *para* substituent of the azo compound and the solvent is stabilized by temperature lowering, which brings about a marked shift of the tautomeric equilibrium in favour of the azo form. The spectra of 1-phenylazo-4-naphthol (Fig. 5), however, indicate that both at room temperature and at −170°C the hydrazone form is also present. The question arises as to by what mechanism the proton transfer from the proton donor substituent in the *para* position to the azo group, resulting in the hydrazone tautomer, proceeds in alcoholic s(l tions.

Consider for our systems the occurrence of the aforementioned equilibrium (*A*) and, in addition, equilibrium (*B*):

$$\mathrm{A—OH + OR_2} \overset{K_4}{\rightleftharpoons} \mathrm{[A—OH\cdots OR_2]} \leftrightarrow \mathrm{A—O^- + HO^+R_2} \overset{K_5}{\rightleftharpoons} \rightleftharpoons \mathrm{H + OR_2} \qquad (B)$$

While equilibrium (*A*) solely has been considered in connection with hydrocarbon solutions, equilibrium (*B*) must be also taken into account in the case of solutions

in aprotic and alcoholic solvents. The contribution of this resonance to the system energy must be first considered. Theoretical analysis reveals that resonance of this kind is only of importance for the strongest and shortest hydrogen bonds. The ion pair formation in Eq. (*B*) thus can be looked upon as an extreme case of a strong hydrogen bonding. Most hydrogen bonds in the ground electronic state, however, are basically electrostatic in nature. This is clearly so also in our case, because if ion pair formation took place, the concentration of the hydrazone form would be determined by the equilibrium K_5 and would increase with increasing hydrogen bonding strength. It was found experimentally, however, that it is the azo form that is stabilized by hydrogen bonding; hence, solute–solvent complexation only occurs according equilibrium K_4 (which is competitive to equilibrium K_1 in Eq. (*A*), ultimately resulting in the hydrazone form). So we suggest that in solutions in aprotic and alcoholic solvents, too, the hydrazone tautomer formation proceeds via dimers of the azo compound.

The fact that for 1-phenylazo-4-naphthol in alcoholic solutions only the azo form and the hydrazone form are observed both at room temperature and at low temperatures, the azo form dimer being absent, indicates that $K_2 \gg K_1$ and the azo–hydrazone ratio is determined by the K_1/K_4 ratio, which obviously depends on the solvent nature and temperature. Since the other compounds examined by us (except for 9-phenylazo-10-hydroxyanthracene) in aprotic or alcoholic solvents are present in their azo forms solely, it follows that either $K_4 \gg K_1$ (which is likely for 4-hydroxyazobenzene) or both K_1 and K_4, though commensurable, are very low (which is likely for the amino derivatives). Our experimental material is insufficient for a quantitative treatment in terms of these considerations.

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