Low-Energy Electronic Spectra of 2-[(4-Sulfanylphenyl)azo]-4,5-diphenylimidazole

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The visible electronic spectra of the title azo compound (HA) in a number of organic solvents have been examined. It was concluded that the compound exists in solutions in an azo \rightleftharpoons hydrazone equilibrium, while in DMF (S) solution the dye exhibits an acid-base equilibrium of the type HA + S \rightleftharpoons A⁻ + HS⁺. The proportional concentration of the conjugate base form A⁻ is largely dependent upon the concentration of the dye, the basicity of the solvent, and the tendency of the ionized form to be stabilized by H-bonding interaction with the solvent molecules. The bands displayed by the different forms of the compound have been assigned to the possible electronic transitions. The visible spectral behaviour of compound in mixed organic solvents has been investigated. The effect of temperature on the compound in DMF at the longer-wavelength visible bands has been also investigated.

Solvents as a medium for chemical and physical processes play an important role and the widespread applications of the azo compounds as dyes, acidbase, redox metallochrome indicators or as histological stains have attracted the interest of many investigators in studies of their spectral properties. In describing the solvent effects, interest has been focused mainly on the polarity effect. In previous communications the spectral characteristics and acid-base properties of a number of arylazo-4,5-diphenylimidazole derivatives are reported [1, 2].

In this paper the experimental work on the spectral behaviour of azo compounds [3-6] continues with a special emphasis on the role of solvent basicity as a factor in the overall effect of solvating capability of the solvent. In this context, this paper presents a study of the spectral behaviour of 2-[(4-sulfanylphenyl)azo]-4,5-diphenylimidazole in organic solvents of different basicity and the effect of temperature on the low-energy band appearing in the basic solvent DMF, as well as a study of the compound in DMF—CCl₄ as a mixed solvent.

EXPERIMENTAL

2-[(4-Sulfanylphenyl)azo]-4,5-diphenylimidazole was prepared as described before [1, 7], the crude compound then being crystallized from aqueous ethanol ($\varphi_r = 1 : 1$) and dried in vacuum over silica gel. The physicochemical properties corresponded with the data given in literature.

All solvents used were spectral grade (BDH or

Merck) products. Stock 1.0×10^{-3} M-solution of the compound in each solvent was prepared in the appropriate volume, more dilute solutions were then obtained by appropriate dilution.

The electronic spectra of freshly prepared solution were recorded on a Shimadzu 2401 PC spectrophotometer containing a thermoelectrically temperaturecontrolling cell holder, within the wavelength range 380 to 700 nm using 1 cm matched silica cells. All measurements were carried out at $(25 \pm 0.1)^{\circ}$ C.

RESULTS AND DISCUSSION

The visible electronic spectra of different concentrations of HA in various organic solvents (acetone, acetonitrile, methanol, dimethylformamide, and carbon tetrachloride) were recorded in the wavelength range $\lambda = 360$ —700 nm. Representative spectra are shown in Figs. 1 and 2. Examination of the results indicates that the visible electronic spectra of HA are largely dependent on both the nature of the solvent employed and the concentration of solute dye. In the less basic solvents, as CCl₄, acetone, acetonitrile, and methanol, the visible spectra of the dyes are characterized by an intense structured band, this band possesses a distinct maximum near 425 nm (cf. Table 1) followed by a shoulder at longer wavelengths. This behaviour is considered as evidence for the presence of this compound [1] in an intramolecular charge transfer, in a tautomeric equilibrium of the azo \rightleftharpoons hydrazone type, which can be represented schematically as follows



Fig. 1. Electronic absorption spectra of HA in DMF. 10^5 $c/(mol dm^{-3})$: 1. 0.20, 2. 0.50, 3. 1.0, 4. 1.5, 5. 2.0, 6. 2.5, 7. 3.0, 8. 3.5, 9. 4.0, 10. 4.5, 11. 5.0, 12. 6.0, 13. 7.3, 14. 8.0.



Thus the shorter-wavelength maximum of the principal band corresponds to absorption by the azo form, and the longer-wavelength maximum (shoulder) corresponds to absorption by the hydrazone form. This assignment is based on the fact that the ground state of the hydrazone form is less stable, and consequently of higher energy than that of the azo form, and in turn low energy is required for excitation in the former case. The visible spectra at low concentration of HA in the basic solvent DMF showed essentially one absorption band in the visible region, this band acquiring a gradual red shift with increasing concentration of HA. At the same time, another band developed in the visible region at shorter wavelength. On further increase in the concentration, the shorterwavelength band becomes higher, while the longerwavelength band reaches a more or less constant value (Fig. 1). It is evident that the shorter-wavelength band reveals two distinct maxima. This behaviour could possibly arise from the existence of this compound in a tautomeric equilibrium of the azo/hydrazone type. On the other hand, the additional longer-wavelength visible band appearing in DMF exceeds by far the polarity effect and could be assigned to absorption by the ionized form of the compound, *i.e.* in this basic



Fig. 2. Electronic absorption spectra of HA in acetone. $10^5 c/(\text{mol dm}^{-3})$: 1. 0.5, 2. 1.0, 3. 1.5, 4. 2.0, 5. 3.0, 6. 4.0, 7. 5.0, 8. 6.0.

Table 1. λ_{max}/nm Values of the Observed Visible AbsorptionBands of HA in Organic Solvents

Form	DMF	MeOH	Acetonitrile	Acetone	CCl_4
Azo Hydrazone Ionized	$430 \\ 470 \\ 525$	430 460 sh	425 455 sh	423 450 sh	420 445 sh

DMF solvent the compound exists in an acid \rightleftharpoons base equilibrium, namely HA + S \rightleftharpoons A⁻ + HS⁺.

This assignment is substantiated by the fact that the band due to A⁻ appears as a single band at very low concentration of HA ($\leq 1.5 \times 10^{-5}$ mol dm⁻³), additionally this band comprises only one maximum indicating that only one species exists. The appearance of this band only in DMF is due to the high basicity (p $K_{\rm s} = 18$) [8] of this solvent relative to acetone (p $K_{\rm s} = 32.5$) [9], acetonitrile (p $K_{\rm s} = 33.3$), and CCl₄.

Evidence for the effect of the basicity of DMF is obtained by recording the spectrum in alkaline DMF (Fig. 3) where the band at \cong 520 nm is observed, while the shorter-wavelength band almost disappears. On the other hand, when a drop of HCl is added to a solution of the compound in DMF (a yellow colour results), only the shorter-wavelength band is displayed.



Fig. 3. Electronic absorption spectra of 3.5×10^{-5} M-HA in: 1. DMF, 2. DMF + HCl, 3. DMF + NaOH.



Fig. 4. Electronic absorption spectra of 3.5 × 10⁻⁵ M-HA in DMF—CCl₄ mixture. c(DMF)/(mol dm⁻³): 1. 1.29, 2. 5.16, 3. 6.45, 4. 7.74, 5. 9.03, 6. 10.32, 7. 11.61, 8. 12.9.

It is evident that HA exists in dilute DMF solution, in the ionic form A^- under the influence of solvent as a proton acceptor.

Accordingly, the longer-wavelength band at \cong 520 nm appearing in DMF solutions is due to absorption by the ionic form A⁻ of the compound.

By increasing the compound concentration in the medium, the possibility of formation of the A^- is lowered, while beyond a certain concentration limit (as noted above) the compound exists in the acid



Fig. 5. Electronic absorption spectra of 3.0×10^{-5} M-HA in DMF at different temperatures $\theta/$ °C: 1. 5, 2. 10, 3. 15, 4. 20, 5. 25, 6. 30, 7. 35, 8. 40, 9. 45, 10. 50, 11. 55, 12. 60, 13. 65, 14. 70, 15. 75, 16. 80.

 \rightleftharpoons base equilibrium. Thus the observed increase in the absorbance of the shorter-wavelength band occurring at 472 nm for concentrated solutions of the compound and at 430 nm by further concentration can be ascribed to absorption by the nonionized form (HA) of the compound. It is to be noted that although DMF and MeOH have a comparable basicity, as their autoprotolysis constants imply $(pK_{s(DMF)} =$ $18.0, pK_{s(MeOH)} = 17.2$ [8, 10], the longer-wavelength band does not appear in methanol. This indicates that not only the basicity of the solvent is responsible for the spectral characteristics of this compound, but also the H-bond acceptor character of DMF, which facilitates the deprotonation of HA, reflecting the role of this dipolar aprotic solvent as an ionizing agent [9]. On the other hand, methanol is known to be a H-bond donor.

This study of the spectra in mixed organic solvents was performed in order to confirm that the presence of HA compound in dilute DMF solution in the ionized form depends upon the basicity of the organic solvent employed [11]. For this purpose the spectra of HA compound in solvents of high basicity such as DMF, each containing successively increasing amounts of less basic solvents, *viz.* CCl₄ have been studied (*cf.* Fig. 4). With the increase in the high basicity (DMF) solvent concentration, the intensity of the main visible absorption band (belonging to absorption of nonionic form) decreases and a new band is developed at longer wavelength, at ≈ 525 nm, *i.e.* ionized form starts to appear as the basicity of medium is getting higher. Generally, the spectra recorded in mixed solvents investigated exhibit a fine isosbestic point. This can be considered as strong evidence for the existence of the HA compound in an acid-base equilibrium in such media.

Evidence for the presence of HA in DMF in an acidbase equilibrium is obtained from studying the visible spectra of a 3.0×10^{-5} mol dm⁻³ solution of HA compound in DMF at different temperatures (Fig. 5). It is apparent that the intensity of the longer-wavelength band (due to absorption by the ionized form) decreases gradually with increasing temperatures, while that of the shorter-wavelength band increases and an isosbestic point is attained. This can be interpreted on the basis of the fact that as the temperature increases, the degree of association of proton to the solvent decreases due to the increased mobility of both. This tends to promote the backward direction of the equilibrium, *i.e.* the ionization of the compound decreases with the increase in temperature. This behaviour confirms the existence of HA compound in an acid-base equilibrium and supports our postulation that DMF has an ionizing effect in such cases.

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