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RESEARCH NOTE

RELATION BETWEEN MOLECULAR STRUCTURE AND SPECTRAL CHARACTERISTICS OF SOME CHELATING MONO-AZO DYES BASED ON *o*-HYDROXY ARYL ALDEHYDES AND CARBOXYLIC ACIDS

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Abstract—The electronic absorption spectra of some chelating mono-azo compounds have been studied in some organic solvents of varying polarities. The u.v. bands in ethanol and cyclohexane are assigned in the light of electronic transitions. The effect of microscopic and macroscopic solvent polarity parameters are also discussed. The i.r. spectra of the solid compounds as KBr discs as well as the ^{1}H NMR spectra have also been assigned and discussed in relation to molecular structure. The azo ⇌ hydrazone tautomerism in some of these compounds is assured. The study indicated that the colour of the materials depends on the polarity and the formation of intermolecular H-bonds with the solvent molecules.

INTRODUCTION

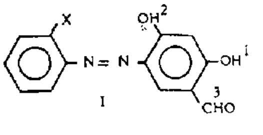
Azobenzenes and their hydrazones find wide application in biological systems and dyeing. The u.v.–visible spectra of azobenzenes and their derivatives have been studied by many workers[1–5]. These studies revealed that the electronic spectra of azobenzenes are affected considerably by changes in the nature, position and number of substituents. TRAVEN *et al.* [3] studied the azo ⇌ hydrazone tautomerism in some dyes based on 2-substituted 1-naphthols; they found that an ester group in position 2-stabilizes the azo tautomer by H-bonding, whereas a COOH or CONHR′ group stabilizes the quinone hydrazone tautomer.

In the present investigation the electronic absorption spectra of some azodyes have been assigned and correlated to the molecular structure. The i.r. spectra of the solid compounds as well as ^{1}H NMR spectra in d^6-DMSO have been recorded and discussed in terms of the molecular structure.

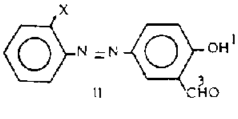
EXPERIMENTAL

Material and solutions

The mono-azo dyes under investigation were prepared by the coupling of salicylaldehyde, salicylic acid, 2,4-dihydroxybenzaldehyde or 2,4-dihydroxybenzoic acid with the diazonium salts of aniline derivatives as described by OSPENSON[4]. The compounds were purified by recrystallization from ethanol, they have the general structural formula:



I



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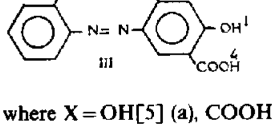

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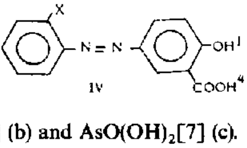


IV

where X = OH[5] (a), COOH[6] (b) and AsO(OH)$_2$[7] (c).

Solutions of the dyes (10^{-3} M) were prepared by dissolving an accurate weight of recrystallized product in the appropriate volume of the pure solvent. Solutions for spectral measurements were obtained by accurate dilution of the stock ones.

Apparatus

The u.v. and visible spectra were recorded by means of a Perkin–Elmer λ-3B spectrophotometer using 1.0 cm matched silica cells. The i.r. spectra were recorded on a Beckmann IR 4220 double beam spectrophotometer while the ^{1}H NMR spectra were obtained with a varian T390-90 A NMR spectrometer using d^6-DMSO as a solvent and TMS as an internal reference.

RESULTS AND DISCUSSION

Tables and figures of spectroscopic data have been deposited with the British Library at Boston Spa, Wetherby, West Yorks, U.K., as Supplementary Publication No. SUP 13507 (9 pp.). Persons wishing to obtain copies of deposited material should write, citing the accession number, directly to Service Enquiries, British Lending Library, Boston Spa, Wetherby, West Yorks LS23 7BQ, U.K.

(i) *Spectra in ethanol and cyclohexane*

The spectra of the azo compounds under investigation were recorded in polar (ethanol) and nonpolar (cyclohexane) solvents in the range 190–550 nm. The spectra of these dyes display mainly three bands (A, B and C). Band (A) in the 204–211 nm region represents the moderate energy π–π^* transition ($^1L_a \leftarrow {}^1A$) of the aromatic system, while band (B) near 265 nm is due to the low energy π–π^* transition corresponding to the ($^1L_b \leftarrow {}^1A$) state. Band (C) on the longer wavelength side is located at 290–380 nm and is sensitive to the solvent polarity. This band can be assigned to an electronic transition involving CT interaction within the whole molecule influenced by the mesomeric interaction between the OH group as a source and the C=O group as a sink.

The CT character of the band can be supported by calculating the E_{CT} values using the following equation [6]:

$$E_{CT} = I_p - (E_A + C). \qquad (1)$$

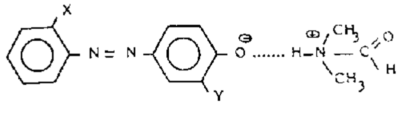
Take the ionization potential (I_p) of OH group as a donor (8.51 eV) and the electron affinity (E_A) of the C=O group as an acceptor (−1.5 eV) and the coulombic force (C) between the electron transfered and the positive hole left behind (5.2–5.6 eV). The E_{CT} values obtained using Eqn (1) amount to 3.81–4.41 eV whereas those obtained practically using the relation:

$$E_{CT} = \frac{1241.728}{\lambda_{nm}(CT)} \text{eV}$$

amount to 3.2–4.28 eV showing satisfactory agreement.

(ii) *Solvent effect*

The spectra of the compounds in organic solvents show a weak shift of the bands due to the π–π^* transitions of the aromatic ring. On the other hand, the CT band shows a wide variation in its position indicating some solvent dependence. In DMF, as a basic high polar solvent, the latter band displays a strong red shift accompained by splitting into two peaks which can be assigned [7] to the strongly solvated and deprotonated molecules. In the latter case a sort of molecular complex is formed through a proton transfer which can be formulated as follows:



Y = CHO or COOH

This type of molecular complex is supported by the great difference in the λ_{max} of the CT band of the compounds in the NHB solvent (ether) than of the HBD solvent (ethanol). To confirm this, the spectra of $\mathbf{II}_c$ and $\mathbf{IV}_c$ are recorded in mixed solvent solutions (ethanol and ether) where the formation constant (K_s) of the molecular complex formed are determined (0.89 and 1.38 respectively) using the method determined by Issa [8], indicating a very labile complex.

To assess the influence of solvents on the CT band, the so called macroscopic and microscopic solvent polarity parameters were applied. The plots of $\Delta\bar{\nu}$ (cm^{-1}) vs $D-1/D+1$ [9] and λ_{max} vs $f(D)$, $\phi(D)$ [10], π, α, β [11], E_T and Z [12, 13] values gave a nonlinear relation. This reveals that these parameters are not the only factors affecting the position of the CT band but the contribution of specific solute–solvent interaction (solvation or more effectively hydrogen bonding between solute and solvent molecules) also takes place. The shift of the CT band is actually the result of changed solvent polarity and the shift due to intermolecular hydrogen bonds formed between the solvent and the azodye molecules.

(iii) *Infrared spectra*

The spectral study of the compounds under investigation is extended to the assignment of i.r. absorption bands using the comparison method followed previously [5, 7]. The spectra show a broad band within the range 3500–3140 cm^{-1} corresponding to ν_{OH}. The low frequency value reveals that the OH group is involved in an intermolecular H-bonding [14]. The i.r. spectra also show a weak band at 3150–3000 and 2980–2900 cm^{-1} regions, which are assigned to the aromatic C–H asymmetric and symmetric stretching vibration respectively. The band representing the symmetric stretching vibration of the N=N group is located at 1405–1450 cm^{-1}. The band due to the C=O appears as a strong one in the range 1700–1635 cm^{-1}. The in-plane deformation vibration of the OH group gives rise to a band appearing in the range 1340–1290 cm^{-1}, while the out-of-plane deformation appears near 875 cm^{-1}. The medium–strong band appearing in the range 1032–975 cm^{-1} is ascribed to the out-of-plane deformation of the isolated C–H of the aromatic system. The weak–medium band at 825–800 cm^{-1} for compounds $\mathbf{II}_{a-c}$ and $\mathbf{IV}_{a-c}$ can be assigned to the out-of-plane C–H deformation vibration of the two adjacent hydrogen atoms. The spectra of compounds **I–IV** display a strong band within the range 770–740 cm^{-1} which is due to the out-of-plane deformation of the four adjacent hydrogen atoms. The bands corresponding to the out-of-plane deformation of the aliphatic C–H group, $\mathbf{I}_{a-c}$ and $\mathbf{II}_{a-c}$ found at 730–710 cm^{-1}. For compounds, $\mathbf{I}_c$, $\mathbf{II}_c$, $\mathbf{III}_c$ and $\mathbf{IV}_c$, the band that appears within the range 810–760 cm^{-1} is due to the As–O bond[15].

The band at 3230 cm^{-1} corresponds to ν_{NH} group while that at 1540–1510 cm^{-1} is due to δ_{NH} supporting the azo$\rightleftharpoons$hydrazone tautomerism.

(iv) ^1H *NMR spectra*

The chemical shift (δ) of the main signals of the ^{1}H NMR spectra of the compounds under investigation were investigated. The signals within the $\delta \simeq 12.10$–10.2 ppm range are removed on deuteration being due to the OH group in *p*- and *o*-position to the azo center. These signals are downfield as a result of their H-bonding. The spectra of compounds $\mathbf{I}_{a-c}$ exhibit a sharp signal in the range 9.85–10.45 ppm that can be assigned to the proton of the aldehydic group. The signal within the range 7.90–8.60 ppm (compounds $\mathbf{III}_{a-c}$, $\mathbf{IV}_a$ and $\mathbf{IV}_b$) is due to the proton of the COOH group in *m*-position to the azo group. Compounds $\mathbf{I}_b$, $\mathbf{II}_b$, $\mathbf{III}_b$ and $\mathbf{IV}_b$ of X =COOH give a signal at 10.2, 11.5, 8.35 and 8.55 ppm respectively. The position of the latter signals at the downfield is attributed to the contribution of the COOH group in an intermolecular H-bonding[16]. The protons of the arsenazo group $AsO(OH)_2$ of the compounds $\mathbf{I}_c$, $\mathbf{II}_c$ and $\mathbf{III}_c$ give rise to a signal at 9.35, 5.25 and 11.5 ppm respectively which disappears on deuteration. Multiple signals of the aromatic protons appear in the range 6.5–7.9 ppm. The signal appearing within the range 11.2–12.8 ppm which is due to the NH proton results from the quenonoid structure supporting the quinone hydrazone$\rightleftharpoons$hydroxy azo tautomerism.

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REFERENCES

[1] M. Gaber, H. A. Dessouki and Y. M. Issa, *Kolorad. Ert.* **1**, 1 (1986).
[2] M. Kamel, M. M. Allam, R. M. Issa, A. T. El-Aref and S. T. El-Aref, *J. prakt. Chem.* **313**, 1131 (1971).
[3] V. F. Traven, A. M. Tsygankova and B. I. Stepanov, *Zh. Org. Khim.* **21** (7), 1539 (1985).
[4] J. M. Ospenson, *Acta chem. scand.* **4**, 1351 (1951).
[5] M. El-Kersh, M. Y. El-Sheikh, R. M. Issa and E. A. Mansour, *Ind. J. Text. Res.* **9**, 70 (1984).
[6] E. M. Kosower and D. C. Remy, *Tetrahedron* **5**, 281 (1959).
[7] M. El-Kersh, M. Gaber, R. M. Issa and I. A. Mansour, *Kolorad. Ert.* **6**, 205 (1983).
[8] I. M. Issa, R. M. Issa, K. A., Idris and A. M. Hammam, *Egypt. J. Chem. Special Issue "Tourky"* 67 (1973).
[9] L. Gati and L. Szalay, *Acta phys. chem.* **5**, 87 (1959).
[10] P. Suppan, *J. chem. Soc.* (*A*) 3125 (1968).
[11] M. J. Kamlet *et al.*, *J. Am. chem. Soc.* **98**, 377, 2885 (1976); *ibid.*, 6027, 8325 (1977).
[12] E. M. Kosower, *J. Am. chem. Soc.* **78**, 5700 (1956).
[13] C. Reichardt, and K. Dimorth, *Fortschr. chem. Forsch.* **11** (1) (1968).
[14] L. J. Bellamy, *The Infrared Spectra of Complex Compounds*, p. 240. John Wiley, New York (1960).
[15] G. Socrates, *Infrared Characteristics Group Frequencies*, p. 145. John Wiley, New York (1980).
[16] L. W. Reeves, *Can. J. Chem.* **38**, 748 (1960).

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