Dyes and Pigments, Vol. 35, No. 3, pp. 289–296, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0143-7208(96)00107-6 0143-7208/97 $17.00+0.00

Solvatochromic Studies on 2-[(2-Hydroxyphenyl)azo]-4-5-diphenylimidazole

A. M. Hammam,[a] N. M. Rageh[b] and S. A. Ibrahim[a]

[a]Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt
[b]Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt

(Received 14 July 1996; accepted 18 September 1996)

ABSTRACT

The visible electronic spectra of the title hydroxyazo compound (abbreviated as HAI) in a number of organic solvents have been studied. It was found that in dilute solutions in basic solvents, HAI exists in an acid–base equilibrium of the type $HAI \rightleftharpoons H^+ + AI^-$. *The proportional concentration of the conjugate base* (AI^-) *in the medium is largely dependent on the HAI concentration, the basicity of the organic solvent and the tendency of stabilization of the* AI^- *form through H-bond interaction with the solvent molecules. The low energy visible band of both the HAI and* AI^- *forms are assigned to a transition involving the whole solute molecule associated with intramolecular CT character. The effect of time on the longer wavelength visible band of HAI has been investigated. © 1997 Elsevier Science Ltd*

Keywords: hydroxyazoimidazole, electronic spectra, solvatochromism.

INTRODUCTION

Solvents as a medium for chemical and physical processes play an important role and the widespread applications of azo compounds as dyes, as acid–base, 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 focused mainly on the polarity effect. In a previous communication [1], we reported on the spectral characteristics and acid–base properties of a number of arylazo-4-5-diphenylimidazole derivatives, and we now extend our experimental work on the spectral behavior of azo compounds [2–4] with particular respect on the role of solvent basicity as a factor in the overall effect of solvating capability of the solvent. In this context, we report here study of the spectral behavior of 2-[(2-hydroxyphenyl)azo]-4,5-diphenylimidazole in solvents of different basicity, and the effect of time on the low energy band appearing in the basic solvent DMF.

EXPERIMENTAL

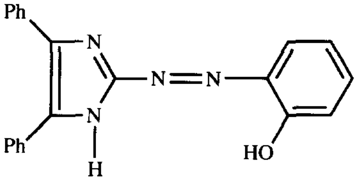
2-[(2-Hydroxyphenyl)azo]-4,5-diphenylimidazole (**1**) was prepared as described before [1, 5], the crude compound then being crystallized from (1:1) aqueous ethanol, and dried *in vacuo* over silica gel. The prepared compound has the following structure.Scheme 1

All solvents used were of spectral grade (BDH or Merck) products. Stock solutions (5.0×10^{-3} M) of the compound in each solvent were prepared in the appropriate volume, more dilute solutions were then obtained by appropriate dilution. The electronic spectra of freshly prepared solutions were recorded on a CECIL 599 spectrophotometer using 1 cm matched silica cells. All measurement were carried out at room temperature (~25°C).

RESULTS AND DISCUSSION

Effect of HAI concentration

The visible electronic absorption spectra of different concentrations of HAI in methanol, acetonitrile, dimethylformamide, acetone and carbon tetrachloride were recorded over the wavelength range 340–720 nm (Figs 1 and 2). Examination of the results obtained reveals that the spectral behavior of HAI is largely dependent on its concentration, as well as on the nature of the solvent employed. The visible spectra at low concentration of HAI in the basic solvent DMF, showed essentially one absorption band in the visible region, this band acquiring a gradual slight blue shift with increasing



I

Scheme 1

concentration of HAI. At the same time, another band developed in the visible region at shorter wavelength. On further increase in the concentration of the compound, the extinction of the shorter wavelength band becomes higher, while that of the longer wavelength band reaches a more or less constant value (Fig. 1). It is evident that the shorter wavelength band is a composite one with two distinct maxima. This behavior could possibly arise from the existence of this compound in a tautomeric equilibrium of the azo⇌hydrazone type [1], namely Scheme 2

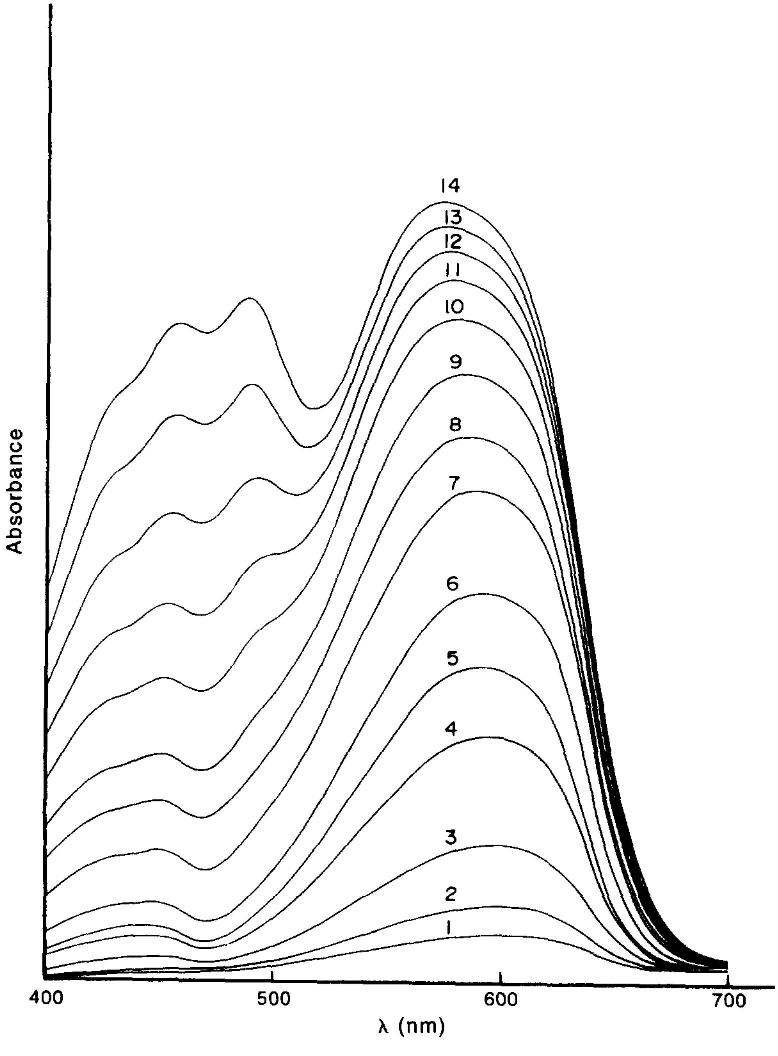


Fig. 1. Electronic absorption spectra of HAI (conc. in M) in DMF: (1) 1.0×10^{-6}, (2) 2.0×10^{-6}, (3) 5.0×10^{-6}, (4) 8.0×10^{-6}, (5) 1.4×10^{-5}, (6) 2.0×10^{-5}, (7) 2.5×10^{-5}, (8) 3.0×10^{-5}, (9) 3.5×10^{-5}, (10) 4.0×10^{-5}, (11) 4.5×10^{-5}, (12) 5.0×10^{-5}, (13) 5.5×10^{-5}, (14) 6.0×10^{-5}.

This is further indicated by the spectral behavior of the compound in other solvents of lower basicity such as methanol, carbon tetrachloride and acetone (cf. Figure 2 as an example), where only the structured shorter wavelength visible band is displayed over a range of concentrations of the compound. This band could, therefore, be assigned to an intramolecular charge transfer transition within both the hydrazone and the azo forms of the molecule. 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 solvent the compound exists in an acid$\rightleftharpoons$base equilibrium, namely

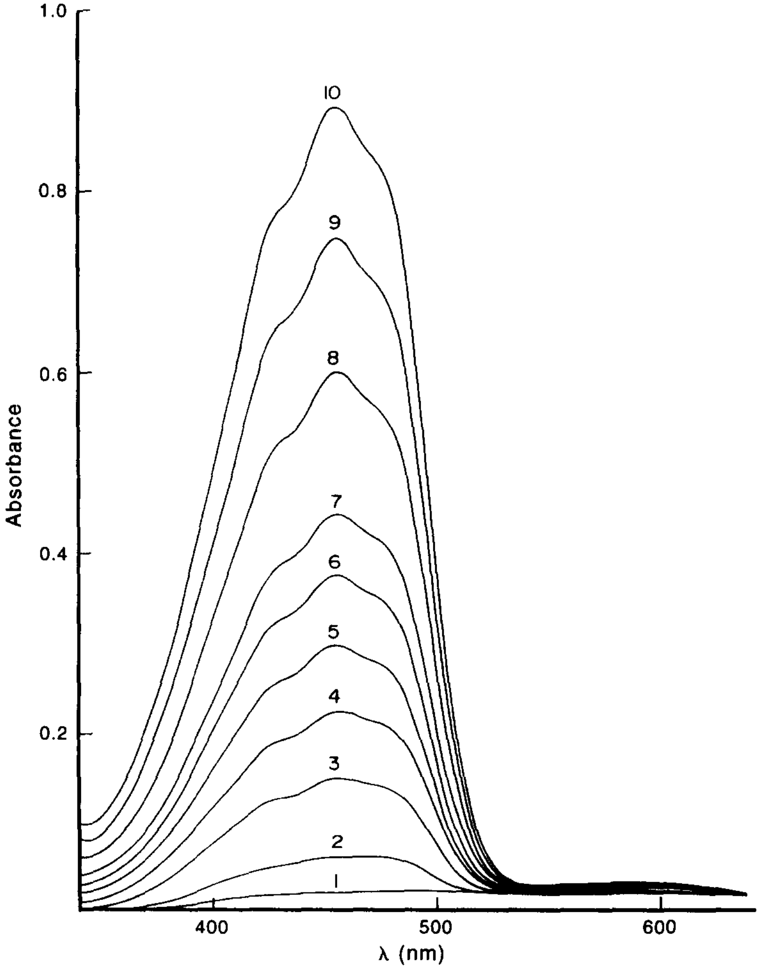
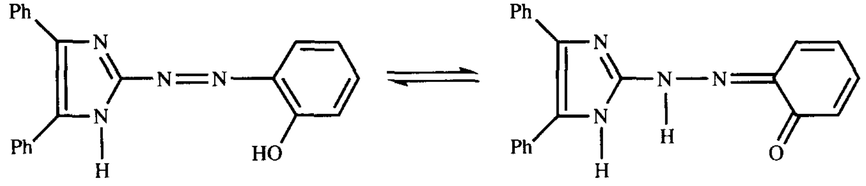


Fig. 2. Electronic absorption spectra of HAI (conc. in M) in methanol: (1) 0.3×10^{-5}, (2) 0.6×10^{-5}, (3) 0.9×10^{-5}, (4) 1.2×10^{-5}, (5) 1.5×10^{-5}, (6) 1.8×10^{-5}, (7) 2.4×10^{-5}, (8) 3.0×10^{-5}, (9) 3.6×10^{-5}, (10) 4.2×10^{-5}.



Scheme 2

$$HAI + S \rightleftharpoons AI^- + HS^+$$

This assignment is substantiated by the fact that the band due to AI^- appears as a single band at very low concentrations of HAI ($\leq 5.0 \times 10^{-6}$ M), 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 ($pK_s = 18$) [6] of this solvent relative to acetone ($pK_s = 32.5$) [7] and CCl_4. Evidence for the effect of the basicity of DMF is obtained by recording the spectrum in alkaline DMF, where a violet color is obtained (Fig. 3)

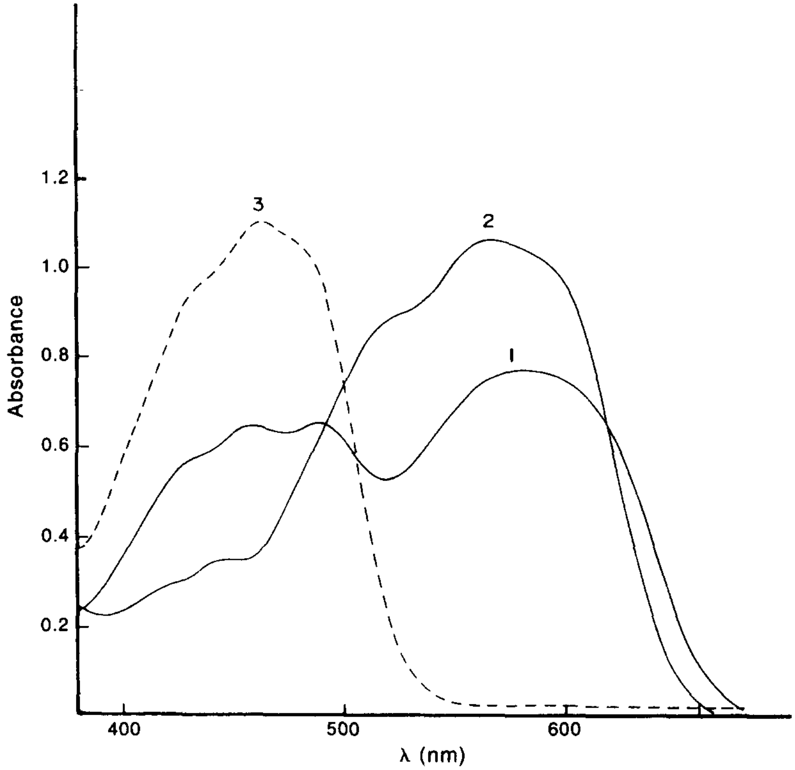


Fig. 3. Electronic absorption spectra of 6.0×10^{-5} M HAI solution: (1) DMF; (2) DMF + NaOH; (3) DMF + HCl.

where the band at ~600 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 color results and only the shorter wavelength band is displayed. It is, therefore, evident that HAI exists in dilute DMF solutions, in the ionic form AI^- under the influence of solvent as a proton acceptor, where

$$HAI + S \rightleftharpoons AI^- + HS^+ (S = DMF)$$

Accordingly, the longer wavelength band at ~600 nm appearing in DMF solutions is due to absorption by the ionic form (AI^-) of the compound (bluish violet colored). By increasing the compound concentration in the medium, the possibility of formation of the AI^- form is lowered, where

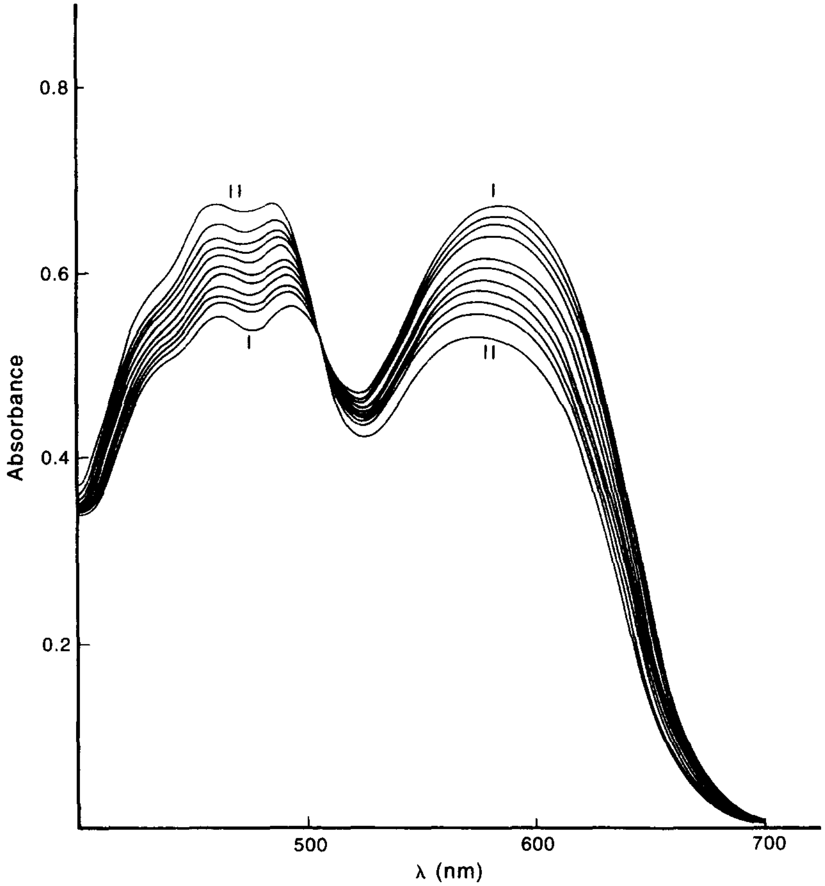


Fig. 4. Electronic absorption spectra of HAI in DMF at different times (min): (1) 0.0; (2) 4.3; (3) 9.0; (4) 13.3; (5) 18.0; (6) 27.0; (7) 31.3; (8) 45.0; (9) 55.0; (10) 70.0; (11) 20.0.

beyond a certain concentration limit (as noted above the compound exists in the acid⇌base equilibrium. Thus the observed increase in the absorbance of the shorter wavelength band occuring at 490 nm for concentrated solutions of the compound (yellow color) can be ascribed to absorption by the non-ionized form (HAI) of the compound. It is to be noted that, although DMF and methanol have a comparable basicity, as their autoprotolysis constants imply ($pK_{DMF}{}^{s} = 18.0$, $pK_{MeOH}{}^{s} = 17.2$) [6, 7], the longer wavelength band does not appear in methanol. This indicates that not only the basicity of the solvent which is responsible for the spectral characteristics of this compound, but also the H-bond acceptor character of DMF, which facilitates the deprotonation of HAI, reflecting the role of this dipolar aprotic solvent as an ionizing medium [8]. On the other hand methanol is known to be a H-bond donor. Evidence for the presence of the HAI in DMF in an acid–base equilibrium of the type $HAI + S \rightleftharpoons AI^- + HS^+$ is obtained from studying the visible spectra of a 5.0×10^{-5} M solution of HAI freshly prepared in DMF over the time range of 0–120 min (Fig. 4). It is apparent that the intensity of the longer wavelength band (due to absorption by the ionized form) increases gradually with time, while that of the shorter wavelength band decreases, and an isosbestic point is attained. This behavior denotes an increase in the extent of ionization with increase in time. This isosbestic point indicates the existence of the acid⇌base equilibrium in both cases.

Band assignment and solvent effect

The λ_{max} values in the visible region of both the HAI and AI^- forms in the various solvents used are listed in Table 1. The visible band relates to

TABLE 1
λ_{max} (nm) Values for the Acid and Base (HAI, AI^-) Forms of HAI in Various Solvents

	λ_{max} (nm)	
Solvent	*HAI*	*AI^-*
DMF	430_{sh} 460 490	600
Acetonitrile	430_{sh} 470	
CCl_4	430_{sh} 470 483_{sh}	
MeOH	430_{sh} 456 476_{sh}	
Acetone	430 458	

absorption by the ionic form AI^- and that corresponding to absorption by the neutral form HAI can be assigned to a transition involving the whole species, associated with intramolecular charge transfer character. It is anticipated that the CT interaction occurs more easily for the AI^- form than within the HAI form. This reflects itself in a lower excitation energy for the CT band of the AI^- form relative to that in the HAI molecule.

REFERENCES

1. Mahmoud, M. R., Hammam, A. M. and Ibrahim, S. A., *Zeitung Physik Chemie (Leipzig)*, **265** (1984) 302.
2. Mahmoud, M. R., Ibrahim, S. A. and Hamed, M. M., *Spectrochimica Acta*, **39A** (1983) 972.
3. El-Gahmi, M. A., Khafagi, Z. A. and Ibrahim, S. A., *Canadian Journal of Applied Spectroscopy*, **36** (1991) 108.
4. Ibrahim, S. A., Hammam, A. M., Kamal El-Dean, A. M., Mohamed, A. A. and Rageh, N. M., *Canadian Journal of Applied Spectroscopy*, **33** (1993) 1.
5. Shibata, S., Furukawa, M. and Nakashima, R., *Analytical Chimica Acta*, **18** (1976) 131.
6. Boyd, R. H., in *Solute–Solvent Interactions*, eds J. F. Coetzee & C.D. Ritchie. Marcel Dekker, New York, 1969, pp. 94–202.
7. Courtot-Coupez, J. & Le Demezet, M., *Bull. Soc. Chim. Fr.* 1033 (1969); see also C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1990, pp. 432–433..
8. Hamed, M. M., Ismail, N. M. and Ibrahim, S. A., *Dyes and Pigments*, **26** (1994) 297.