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A NEW ASPECT OF AZO-HYDRAZONE TAUTOMERISM

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Abstract—Structures of 3,5-dimethoxy-4-hydroxyazobenzene and of a new parent compound, 2,6-dimethoxy-4-hydroxyazobenzene, are investigated. Owing to their very high solubility it was possible to proceed to a comparison of the UV, ^{1}H NMR and ^{13}C NMR data for the same solvent. Symmetric substitution by two OMe groups in the ring bearing the OH group results in the isolation of the azo or hydrazone tautomer, using the available positions of substitution. The usefulness of the ^{13}C NMR technique in the investigation of azo-hydrazone tautomerism is underlined.

The study of hydroxy azo compounds has been of great value for the theoretical understanding of a phenomenon widely encountered in chemistry: tautomerism.

Since the work published by Zincke and Bindewald,[1] the azo-hydrazone tautomerism has been investigated by numerous workers with a view to (i) prove the existence of an equilibrium, if any (almost all the available spectroscopic methods have been used), (ii) investigate the influence of factors such as: substituent, solvent, temperature, (iii) to gain an understanding of the (non) existence of such a thermodynamic equilibrium. Two recent publications sum qualitative and quantitative information available on this subject.[2,3]

The present paper deals with an aspect of this phenomenon which has been disregarded until now: the substitution of the ring carrying the OH group and its effect on the relative stability of the tautomers. Results of such an approach are reported with respect to the following compounds.

EXPERIMENTAL RESULTS

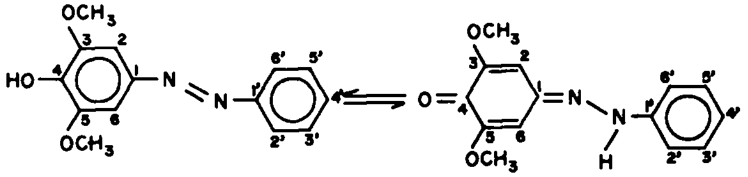
1. *UV data.* Figure 1 shows the UV spectra of both compounds determined in an inert solvent: cyclohexane. Significant differences are displayed concerning the wavelength of the main peak (I: 364 nm; II: 400 nm) and the shapes of the absorption curves. Moreover, inspection of Table 1 shows that ϵ_{max}(II) is nearly double than ϵ_{max}(I).

2. *NMR of* ^{1}H *and* ^{13}C. Fortunately, the compounds are soluble enough to make possible a structure analysis using NMR spectroscopy. A survey of data reported in Tables 2 and 3 shows clearly that I and II possess quite different structures; the main differences concern the labile hydrogen (^{1}H) and the carbon linked to the oxygen (^{13}C).

DISCUSSION

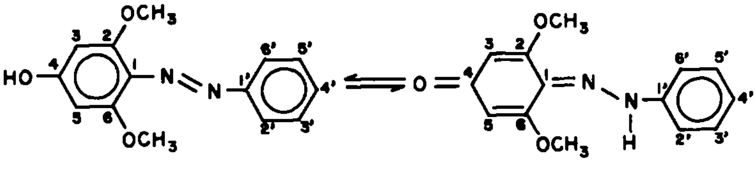
The experimental data reported above can be interpreted only by assigning an azo structure to I, as opposed to an hydrazone structure of II.

This interpretation will be discussed in the light of the spectroscopic data.



I(A) I(H)

3,5-dimethoxy-4-hydroxyazobenzene



II(A) II(H)

2,6-dimethoxy-4-hydroxyazobenzene

In the first place, the UV absorption profile for I is a typical of the azoic structure: an intense transition at $\lambda \simeq 370$ nm of the $\pi \rightarrow \pi^*$ nature ($\epsilon = 20{,}000$) and a shoulder at a longer wavelength due to the $n-\pi^*$ transition of the -N=N- linkage.§

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§By comparing these values of λ, ϵ with those of classical azoic compounds,[4] it can be deduced that the two OMe groups infer only a slight red shift of the transitions.

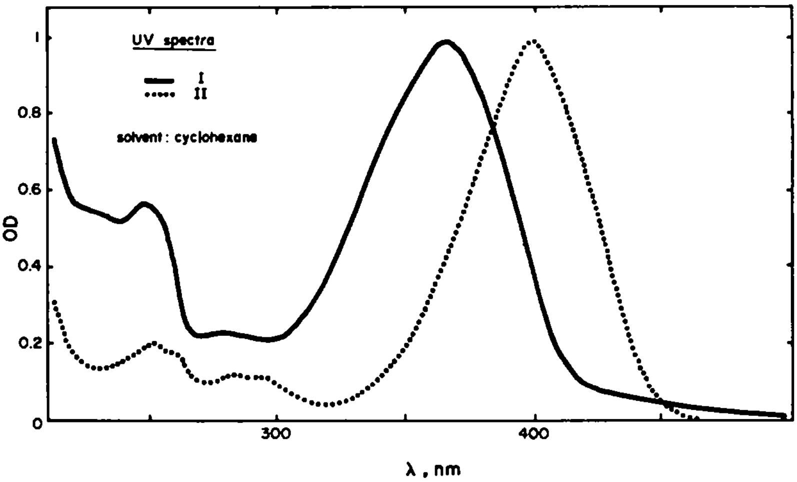


Fig. 1. UV absorption spectra of compounds I and II (I: 5.13×10^{-5} M/l; II: 2.56×10^{-5} M/l).

Table 1. UV spectra data for compounds I and II

	(I)		(II)	
Solvent	λ_{max} (nm)	ε_{max}	λ_{max} (nm)	ε_{max}
Cyclohexane	364	19,500	400	39,000
Benzene	370	18,500	408	38,500
Dioxane	374	18,500	404	38,000
Chloroforme	368	18,500	409	41,000
Dichloromethane	366	18,000	411	41,500
Acetonitrile	369	18,500	406	40,000
Methanol	370	18,500	420	40,000

In contrast, compound II presents a single and more intense transition: no shoulder is to be observed and this fact is typical of an hydrazone structure.[5]

The significant difference between the NMR signals related to the labile proton precludes any doubt on the possible structures: the low-shift signal is to be ascribed to an O–H bond and the high shift signal to an N–H bond; this is in keeping with previous results reported on azo-hydrazone tautomerism by Saeva.[6] Moreover, the large difference between the chemical shifts of H_2 proton (7.3) in I and H_3 proton (5.3) in II can be related to the lack of *ring current* in compound II.

Table 3. ^{13}C chemical shifts in ppm/TMS (solvent: $CDCl_3$ at 310 K). The proposed assignment is based on the examination of the C–H coupling

n°	AZOBENZENE	p-METHOXY AZOBENZENE	I	II	II*
1		147.2	145.6	122.1	122.5
2 6		124.9	100.8	162.5 160.1	161.3
3 5		114.3	147.4	102.7 101.5	102.0
4		162.2	138.3	186.2	186.1
1'	152.5	153.0	152.7	142.6	142.7
2'-6'	122.7	122.7	122.6	115.3	115.5
3'-5'	128.8	129.1	129.1	129.5	129.6
4'	130.7	130.5	130.5	124.3	124.5

*with addition of HCl

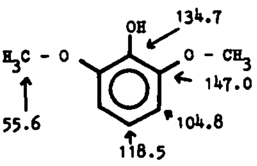


Table 2. ^1H RMN data (solvent: $CDCl_3$)

Compound I		Compound II	
δ (ppm/TMS)		δ (ppm/TMS)	
3.95	s (6H ; CH_3, CH_3)	3.6	s (6H ; CH_3, CH_3)
7.3	s (2H ; H_2, H_6)	5.3	s (2H ; H_3, H_5)'
7.4 - 7.5 7.8 - 7.9	m (3H m (2H ; C_6H_5)	6.8 - 7	m (5H ; C_6H_5)
5.1 - 5.2	m (1H ; OH)	10.4	m (1H ; NH)

^{13}C NMR offers a decisive proof: the chemical shift (138.3) of carbon 4 in compound I is close to the value for the carbon-bearing hydroxyl group in 2,6-dimethoxyphenol (134.7), whereas in compound II, the chemical shift (186.2) corresponds to that of a quinonoid carbonyl group (187.0 for *p*-benzoquinone).

Finally, it should be noted that:

(a) In the case of I, the peaks related to the C atoms of the unsubstituted ring are very similar to those of azobenzene and *p*-methoxy azobenzene;

(b) On the other hand, these C atoms in II exhibit significant differences with those of azobenzene and *p*-methoxyazobenzene.

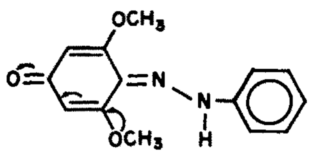
This can be explained by the fact that the lone nitrogen pair of electrons conjugates with the unsubstituted ring and thus 2′ and 4′ atoms are more shielded.

From inspection of Table 3 it should be noted that in the case of II carbons 2 and 6, respectively 3 and 5, show distinct signals. This fact can be related to the relatively high barrier of isomerization surrounding the –C=N bond; moreover, with addition of HCl trace amounts this splitting disappears, owing to the catalytic effect of the H^+ ions resulting in a considerable lowering of the isomerization energy barrier, hence the coalescence of the concerned peaks.

The nature of the compounds being elucidated, the possible occurrence of tautomerism may be considered. From the UV data reported in Table 1 it may be inferred that the main transition for I and II undergoes a positive solvatochromy and the shifts may be readily interpreted in the classical quantum mechanical treatment of the solvent effect. Moreover, neither modification of the absorption profile nor significant variation of the absorption coefficient ϵ was observed as the solvent is varied.

In addition, variation of temperature did not affect the spectra. Thus, at ambient temperature, the equilibrium is entirely shifted towards azo and hydrazone forms for I and II, respectively, a conclusion supported by the NMR spectra.

It is noteworthy that the two possible symmetric substitutions by OMe groups *freeze* each of the tautomers. This original result may be interpreted by the donor ability of the OMe group, which results in a stabilization of the hydrazone tautomer II, according to the following scheme:



Such a mesomer effect is not possible for hydrazone I, hence the opposite result for this compound.

It was also possible to underline the different behaviour of these tautomers when submitted to light excitation.

(a) I undergoes a normal *trans* → *cis* isomerization, followed by a first order relaxation;

(b) No transient in benzene, dioxane, acetonitrile, methanol ($\tau > 10\ \mu s$) could be observed for II by flash photolysis. Moreover, no photochromic behaviour in this time scale was detected on parent compounds: the hydrazone tautomer of 4-phenylazo-1-naphthol and equally the 1,4-naththoquinone-N-methylphenyl hydrazone.[5] This warrants the generalization of the absence of the *trans* → *cis* isomerization ($\tau > 10\ \mu s$) for the hydrazone tautomer of *p*-hydroxazoic compounds: this is most important for the interpretation of the photochromism exhibited by these compounds, particularly when both tautomers are present prior to light excitation.

CONCLUSION

Using UV, ^1H and ^{13}C NMR it was possible to underline the non-trivial role of symmetric substitution by two OMe groups in the ring bearing the OH group, in the case of *p*-hydroxy azobenzene: 3,5 substitution leads to an azo structure and 2,6 substitution to an hydrazone one, the tautomerism equilibria being in both cases totally displaced irrespective of the solvent. This allowed to investigate for the first time some properties of an hydrazone structure that displays neither any substituent in the benzene ring without OH nor any Me group at the NH atom.

EXPERIMENTAL

UV spectra were recorded on a Cary 15 spectrophotometer, ^1H spectra on a Varian 60 and ^{13}C spectra on a Bruker WP 80.

Synthesis of compound I. 0.025 mole of 2,5-dimethoxyphenol and 2.5×10^{-3} moles of pyridine were dissolved in 20 ml EtOH. The mixture was cooled to −10°. Diazonium salt was added and reacted during 30 min. The soln became brown and was cooled to −30°: a ppt appeared; after water washing and drying, a recrystallization from glacial AcOH gave I: f.p. 137° (138°[7]). $C_{14}H_{14}N_2O_3$: C, 65.10% (65.17%); H, 5.46% (5.53%); N, 10.85% (10.65%).

The preparation of II. Following the above procedure with 3,4-dimethoxyphenol this was unsuccessful. 0.025 mole of 3,4-dimethoxyphenol and 2.5×10^{-3} moles of pyridine were dissolved in 50 ml EtOH. The mixture was cooled to −10° and diazonium salt was added: an orange ppt appeared immediately. This ppt was recrystallized in 150 ml distillated water with 10 ml of N Na_2CO_3. After cooling, the ppt was yellow; filtration and drying at 80° (during 12 hr) led to II: m.p. 155°. $C_{14}N_{14}N_2O_3$: C, 65.10% (65.0%); H, 5.46% (5.34%); N, 10.85% (11.01%).

REFERENCES

[1] T. Zincke and H. Bindewald, *Chem. Ber.* 17, 3026 (1884).

[2] I. Y. Bershtein and O. F. Ginsburg, *Russ. Chem. Rev.* 41, 97 (1972).

[3] S. Patai, *The Chemistry of the Hydrazone, Azo, Azoxy Groups*, Chap. 18. Wiley, New York (1975).

[4] K. Hirayma, *Handbook of UV Spectra of Organic Compounds.* Plenum Press, New York (1967).

[5] P. Jacques, Thesis, Mulhouse (1977).

[6] F. D. Saeva, *J. Org. Chem.* 36, 3842 (1971).

[7] V. Ettel and J. Hebky, *Coll. Czech. Chem. Comm.* 15, 639 (1950).