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HMO CONSIDERATION OF FACTORS AFFECTING TAUTOMERISM IN HYDROXYARYLAZO COMPOUNDS

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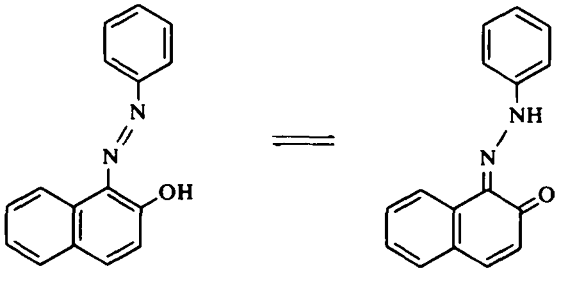
Abstract—The factors affecting tautomeric equilibrium of hydroxyarylazo compounds have been treated by the HMO method using difference in bonding energy as criterion of tautomeric stability. The larger the ring bearing the oxygen atom, the more stable is the hydrazone tautomer. By the same approach, it is further shown that intermolecular and intramolecular hydrogen bonding, electron withdrawing substituents, and the formation of hydrogen-bonded dimers favor the hydrazone tautomer.

INTRODUCTION

THE PHENOMENON OF TAUTOMERISM in hydroxyazo dyes has been known for some time and has been studied by numerous workers by such means as IR[1–3] UV–vis,[4–8] and NMR[3, 9–11] spectroscopy. These studies have shown the importance of solvent, substituents and ring size on the equilibrium between azo and hydrazone forms. Spectral assignments have not always been unequivocal, however, and various authors have disagreed as to which tautomer predominates under given conditions. Because of the importance of this class of compounds as commercial dyestuffs, it is important to understand the factors which control the position of the tautomeric equilibrium from a quantum chemical viewpoint. The effect of variation in aromatic ring size is considered first; then, for the case of 1-phenylazo-2-naphthol (shown below), the effects of hydrogen bonding, solvent interactions, substituents and dimer formation are considered.



azo hydrazone

METHOD

To establish the relative stability of the tautomeric forms within the framework of the Hückel molecular orbital (HMO) method,[12] use has been made of the concept of bonding energy, defined by the equation[13]

$$BE = W - W'$$

where W is the total π-electron energy and W' is the energy of π-electrons localized on atomic p-orbitals. That is

$$W' = \sum_{i=l}^{n} s_i\alpha_i$$

where n is the number of atomic centers, s_i is the number of electrons contributed by atom i to the π system, and α_i is the Coulomb integral for atom i. The BE quantity appears better founded[13–15] than the often used delocalization energy[12] in view of the uncertainty in defining the correct Kekulé structures. For a given tautomeric pair it is sufficient to compare the bonding energies of two tautomers, while for systems differing in ring size, bonding energy per π electron, BE/n, is more appropriate. The tautomer with the greatest bonding energy or bonding energy per electron is then expected to have the greater stability.

In applications of the HMO method the Coulomb and resonance integrals for heteroatoms, α_x and β_{xy}, are expressed in terms of standard values for all-carbon systems by the relationships[12]

$$\alpha_x = \alpha + h_x\beta$$

$$\beta_{xy} = k_{xy}\beta$$

Pi-energies and bonding energies are then given in terms of the carbon–carbon resonance integral, β. For a comparison of bonding energies of two tautomers, then, use of appropriate values for h_x and k_{xy} is critical, especially in the present case where calculations on an azo-hydrazone pair requires a choice of twelve heteroatom parameters. The values used in this work are based on those given by Streitwieser;[12] the values for the azo group have been successfully used by Bock.[16] The resonance integrals for the C—NH and NH—N bonds in the hydrazone tautomer are those used by Barltrop and Conlong,[17] who point out that since the hydrazone is non-planar, resonance integrals for these bonds will be lower than those derived from studies of planar conjugated systems. In Table 1 are summarized the values of heteroatom parameters used in this work. Some variation in parameters was tried, however those shown gave results most consistently in agreement with experiment.

TABLE 1. HMO HETEROATOM PARAMETERS USED IN STUDY OF AZO-HYDRAZONE TAUTOMERISM[a]

Azo		Hydrazone	
h_N	= 0·50	h_{NH}	= 1·50
h_O	= 2·00	h_N	= 0·50
k_{CN}	= 0·90	h_O	= 1·00
k_{NN}	= 1·00	k_{CN}	= 0·70
k_{CO}	= 0·80	k_{NN}	= 0·70
		$k_{C=N}$	= 1·10
		k_{CO}	= 1·00

[a] From refs 12, 16 and 17.

RESULTS

Variation in aromatic rings. Of the several factors influencing the position of the azo-hydrazone equilibrium, the first to be considered by this method is variation in size of the aromatic rings comprising the two halves of the hydroxyarylazo system.

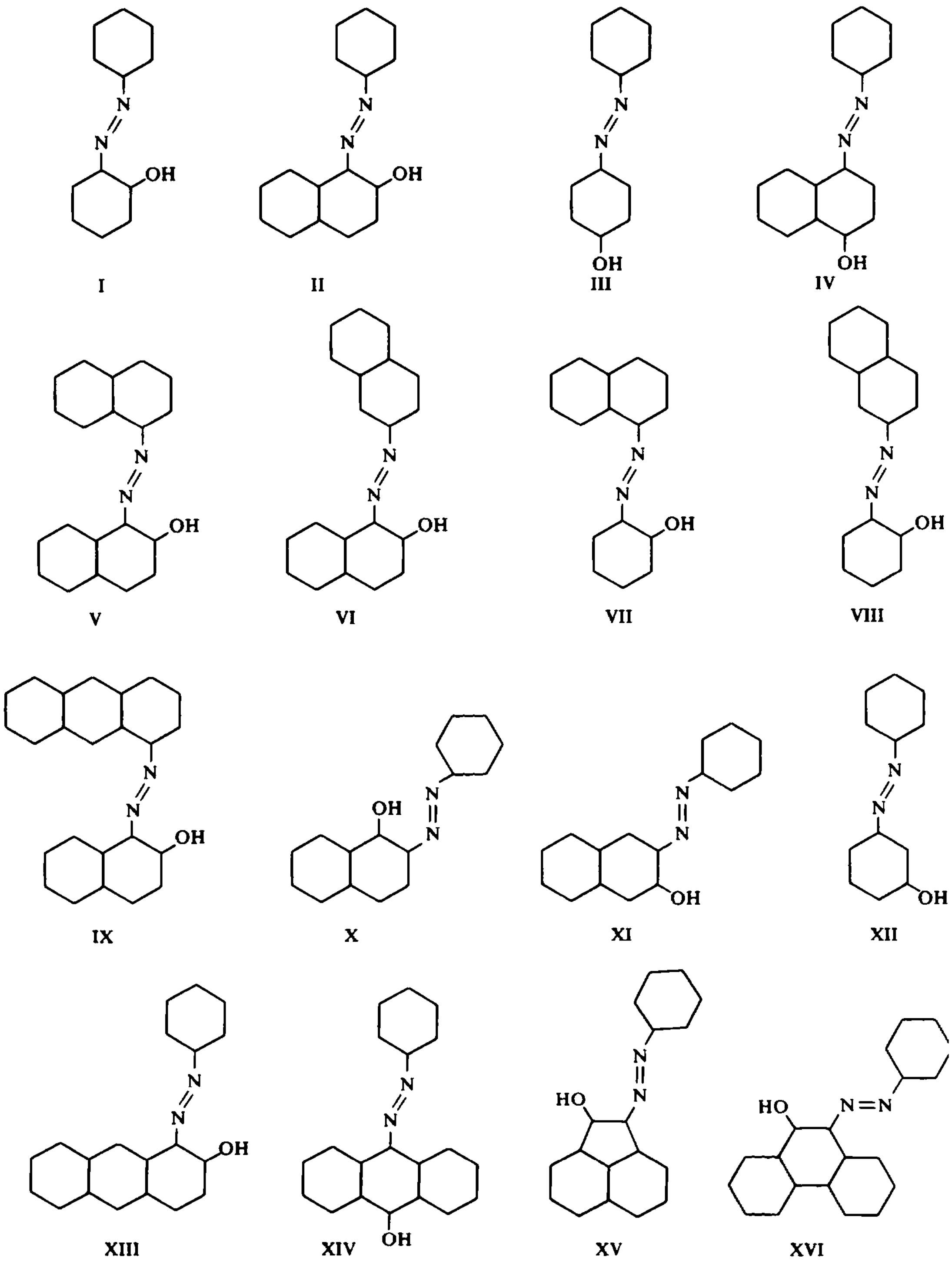


FIG. 1. Azo compounds with varying ring size.

Bonding energies and bonding energies per electron were calculated* for compounds I–XVI shown in Fig. 1 with the differences ΔBE_{A-H} and $\Delta(BE/n)_{A-H}$ being presented in Table 2. (The structures of I–XVI are shown as azo tautomers for convenience without implying anything about the major tautomer.) A positive value of ΔBE_{A-H} or $\Delta(BE/n)_{A-H}$ indicates greater stability for the azo form, while a negative value indicates greater stability of the hydrazone tautomer. Where experimental evidence is to be found in the literature, this is also shown in Table 2. In general, the results are in agreement with experiment for compounds already studied.[1–11] All the azophenols are shown to be more stable in the azo form. The azonaphthols are indicated to be more stable as the hydrazone tautomers, with the exception of 3-phenylazo-2-naphthol. The fusion of a third ring to the portion of the molecule bearing the oxygen atom is expected to further stabilize the hydrazone form, while the size of the aromatic ring

TABLE 2. BONDING ENERGY DIFFERENCES AND OBSERVED MAJOR TAUTOMER FOR AZO-HYDRAZONE PAIRS

Compound	ΔBE_{A-H}[a]	$\Delta(BE/n)$[a]	Major tautomer[b]	Phase[c]	Method	Ref.
I	0·069	0·004	A	M, E	UV	6, 8
			A	N	IR	1
II	−0·052	−0·002	A	H	UV	4
			H	E	UV	4, 8
			H	C, N	IR	3, 2
			H	Ch	NMR	3, 8, 9
III	0·082	0·005	A	N	IR	1
			A	E	UV	8
IV	−0·054	−0·002	A	Ch	NMR	11
			A	H, M, E	UV	4, 5, 8
			H	E	UV	4, 5
			H	N	IR	2
V	−0·036	−0·001				
VI	−0·049	−0·002				
VII	0·083	0·004				
VIII	0·071	0·004				
IX	−0·032	−0·001				
X	−0·044	−0·002	H	M, P	UV	6
			H	Ch	IR, NMR	3
XI	0·129	0·007	A	M	UV	6
			A	Ch	IR	3
XII	0·255	0·016	A	M	UV	6
XIII	−0·096	−0·003	H	E	UV	8
XIV	−0·228	−0·009				
XV	−0·204	−0·009				
XVI	−0·127	−0·006				

[a] In β-units

[b] A = azo; H = hydrazone

[c] M = methylcyclohexane; E = ethanol; N = nujol; H = hexane; C = carbon tetrachloride; Ch = chloroform or deuteriochloroform; P = propanol.

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* Calculations were performed using an HMO program written in FORTRAN IV for the XDS Sigma 7 computer.

in the other portion of the molecule is indicated to have less of an effect. A comparison of the calculated energy terms with the results of experiment suggests that when $|\Delta(BE/n)_{A-H}| > 0{\cdot}002\beta$, then only one tautomer should be present.

Hydrogen bonding. The effects of hydrogen bonding are considered by Pullman and Pullman[18] to be sufficiently well established to be included within the HMO framework. According to this treatment, for a hydrogen-bonded system, X—H ······ Y, the following HMO parameters obtain:

$$\alpha_{XH} = \alpha_X - 0{\cdot}2\beta$$

$$\alpha_{Y \cdots\cdot H} = \alpha_Y + 0{\cdot}2\beta$$

$$\beta_{X(H)Y} = 0{\cdot}2\beta$$

Thus, the effective electronegativity of atom X is decreased by hydrogen bonding and that of Y is increased. Allowance is also made for electronic interaction between atoms X and Y, presumably π delocalization *via* the 2p orbital on hydrogen.

In the case of 1-phenylazo-2-naphthol the result of intramolecular hydrogen bonding is the formation of a pseudo-aromatic sextet, a concept qualitatively discussed by Shigorin.[19,20] The effect on the stability of the two tautomers as indicated by the BE criterion is shown below:

	Bonding energy, β	
	Azo	Hydrazone
No H-bond	24·670	24·722
With H-bond	24·773	24·972

The effect of intramolecular hydrogen bonding on this system is thus to increase the stability of both azo and hydrazone tautomers. The added stability for the hydrazone, however, is over twice that for the azo form, a conclusion which is consistent with the results of visible and Raman spectroscopic studies on ionic arylazonaphthols.[21]

It is a simple extension to consider the effects of intermolecular hydrogen bonding, and thus to treat the effects of solvent on the position of the tautomeric equilibrium. In this case for centers XH and Y interacting with hydrogen-bonding solvents we have:

$$\alpha_{XH \cdots\cdot SH} = \alpha_X - 0{\cdot}2\beta$$

$$\alpha_{Y \cdots\cdot H-S} = \alpha_Y + 0{\cdot}2\beta$$

Such an approach to solvent effects has been used to correlate differences in ESR spectra of semiquinone radicals seen in varying solvents.[22,23]

The effect of hydrogen bonding by solvent to 1-phenylazo-2-naphthol in terms of bonding energies of the two tautomers is shown below:

	Bonding energy, β	
	Azo	Hydrazone
No H-bond	24·670	24·722
Solvent H-bond	24·717	24·899

As is the case for intramolecular hydrogen bonding, the effect of intermolecular hydrogen bonding is seen to be a stabilization of both azo and hydrazone tautomers, with over three times the added stability resulting in the case of the hydrazone tautomer. (The amount will, in fact, depend on the strength of the solvent-solute interaction, i.e. how large is the perturbation to the Coulomb integrals of atoms X[H] and Y.) Interestingly, the results of similar calculations on 4-phenylazo-1-naphthol were almost identical to those shown there for 1-phenylazo-2-naphthol. It seems likely that the criterion of $\Delta BE/n = \pm 0{\cdot}002\beta$, used in considering compounds with varying ring size, implicitly contains intramolecular hydrogen bonding terms. It is not certain, therefore, whether this value may be used to predict tautomeric stability of *para*-hydroxyazo compounds where such intramolecular hydrogen bonding is not possible.

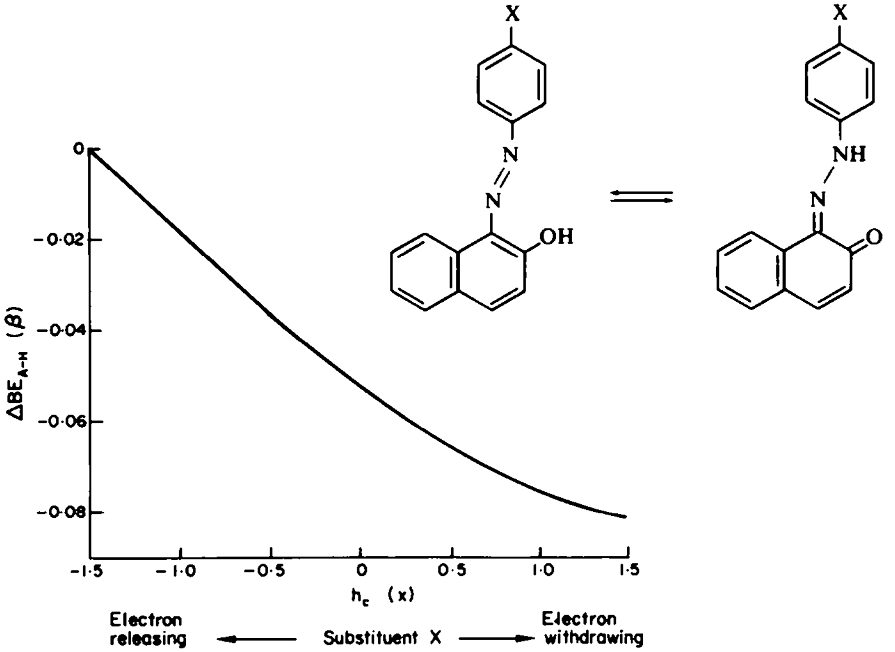

FIG. 2. Effect of substituents on azo-hydrazone equilibrium.

Substituents. In addition to the effects of ring size and nature of solvent, the attachment of various substituents is known to affect the position of the azo-hydrazone equilibrium. As a first-order approach to the effects of substituents, one may vary the Coulomb integral of the carbon atom to which the substituent is attached as suggested by Peters[24] according as the substituent is electron withdrawing or releasing. Strictly speaking, this approach neglects conjugative effects of the substituent and treats only the inductive effect, but for the purpose of defining trends this is sufficient.

In the present study, the effect of varying substituents X in 1-(*p*-X-phenylazo)-2-naphthol on the position of the tautomeric equilibrium were considered. The results of this investigation are summarized in Fig. 2, which shows the difference in bonding energy (ΔBE_{A-H}) as a function of the electron-donating or withdrawing ability of the substituent. From this it is seen that as the Coulomb integral of the substituent bearing carbon atom is varied from $-1{\cdot}5$ (electron releasing) to $+1{\cdot}5$ (electron withdrawing), the stability of the hydrazone tautomer increases. This is precisely what is seen experimentally.[2,4]

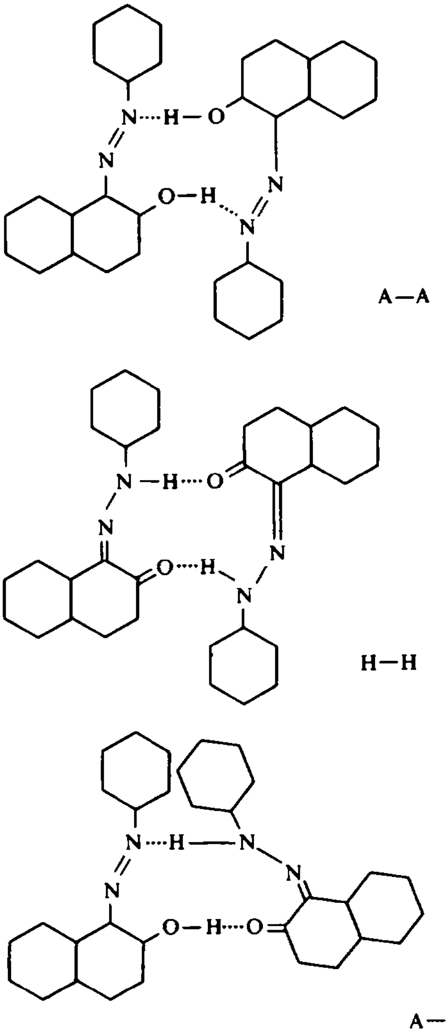

FIG. 3. Possible hydrogen-bonded dimers of 1-phenylazo-2-naphthol.

Dimer formation. Recent work[25,26] has shown that arylazo-naphthols readily form dimers and higher aggregates in solution. The possibility of hydrogen bonded dimers was, therefore, examined from the HMO viewpoint. The three cases considered, shown in Fig. 3, are the azo-azo(A-A; two N · · · · H—O bonds), the hydrazone-hydrazone (H-H; two O · · · · H-N bonds), and the azo-hydrazone dimer (A-H; one N · · · · H-O and one O · · · · H-N bond).

The *BE*'s for these three cases are: A-A, $49{\cdot}456\beta$; H-H, $49{\cdot}815\beta$ and A-H, $49{\cdot}636\beta$.

Now the bonding energies of the azo and hydrazone monomers are respectively 24·670 and 24·722β, so that the extra stability due to dimer formation is 0·116β for the A–A case, 0·371β for the H–H case and 0·244β for the A–H mixed dimer. The added stability for the H–H dimer is three times that of the A–A dimer, so that dimerization is expected to favor the hydrazone tautomer. This π-stabilization is in addition to differences in electrostatic attraction in comparing the more polar hydrazone to the azo tautomer. The A–H mixed dimer is considered unlikely because of steric crowding by the two phenyl groups.

DISCUSSION

In the present study, a number of different factors affecting azo-hydrazone tautomerism have been considered* within a single framework using the criterion of bonding energies for judging stability. When variation in sizes of the two aromatic rings is considered, a difference in bonding energy per electron in excess of 0·002β leads to the expectation that only one tautomer will be seen. For compounds with $\Delta(BE/n)$ within the range of ±0·002β it is expected that either or both members of the tautomeric pair will be seen under varying conditions of solvent or temperature.

A further generalization from a consideration of azo compounds with various aromatic rings is that it is the size of the ring which bears the oxygen atom rather than the other ring which determines the position of the tautomeric equilibrium. Ospenson[8] considered that the hydrazone grouping (C—NH—N═C—C═O) is inherently more stable than the azo system (C—N═N—C═C—OH) and that this factor is modified by the stability of the quinone portion. In the present study the two tautomers have not been disected into their constituent parts, but rather each considered as a whole and their bonding energies compared. The criterion of bonding energies makes no distinction between the relative stabilities of the *ortho* and *para* isomers, while in fact such differences exist.[11] The reason for this lies in the fact that we are considering a π energy term and make no allowances for difference in σ-energies, solvation energies and non-bonded interactions. While a consideration of π bonding energies alone is sufficient to account for the observed equilibria in most cases, these other factors do indeed play a role.

When hydrogen-bonding effects are considered, the inherent stability of the hydrazone is further enhanced. This occurs both for intra- and intermolecular hydrogen bonds. The hydrogen-bonded H—H dimer shown may be seen in solution spectra,[25, 26] while preliminary x-ray crystallographic studies within these laboratories[27] have shown that this is the arrangement of 1-phenylazo-2-naphthol in the solid state. It is probable that when both azo and hydrazone species can be seen in solution, then from a bonding energy criterion, only the hydrazone may be expected in the ordered solid (*i.e.* with intermolecular H-bonding).

While the calculation of exact azo-hydrazone equilibrium constants is too much to expect from a Hückel-type approach, it is, nonetheless, gratifying to note that the experimental trends are reproduced by this method.

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* As pointed out by a referee, an additional factor might be the effect of rotation about the N—N bond. Although not considered in this work, such an effect would become operative with the steric effects of nearby substituents.

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