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Theoretical Investigations on the Tautomerism of 1-Phenylazo-4-naphthol and its Isomers

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ABSTRACT

The azo-hydrazo tautomerism of three dyes, viz., 1-phenylazo-4-naphthol, 1-phenylazo-2-naphthol and 2-phenylazo-1- naphthol was investigated using quantum chemical AM1 and ab-initio methods. The effect of the substituents in the phenyl ring is rationalised in terms of the HOMO–LUMO molecular orbital diagrams of both tautomeric forms. A relation between the computational results and the experimentally obtained tautomeric ratios in different solvents was found. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

A basic structural requirement for prototropic tautomerism is the presence of a labile proton in the molecule. This requirement is manifested in the case of azo dyes containing an OH group conjugated with the azo group and these dyes exist as a tautomeric azo-hydrazo mixture both in solution and in the solid phase. Since the tautomeric ratio is a quite important parameter for the industrial application of such dyes, investigations of the azo-hydrazo tautomerism are of interest both from theoretical and practical aspects. It should be noted that a statistical evaluation has shown a substantially high theoretical possibility for tautomerism, as much as 92%, for the monoazo dyes whose structures have been published in the Colour Index [1].

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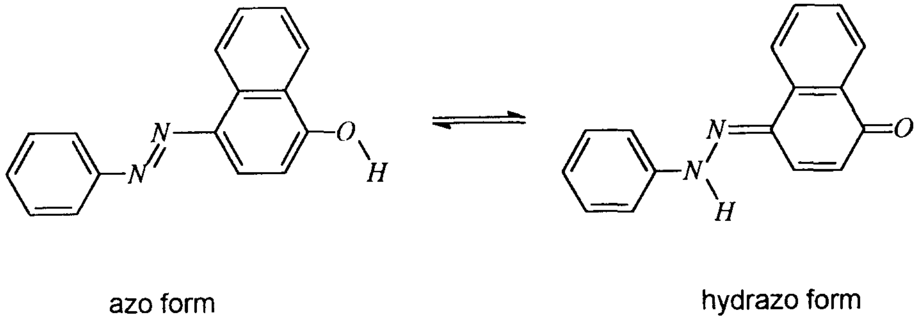
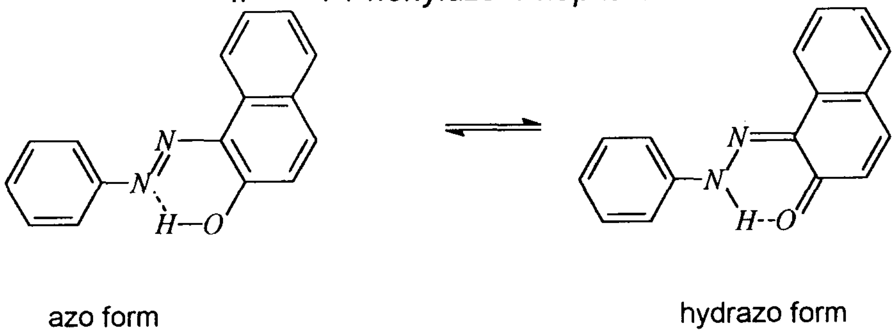
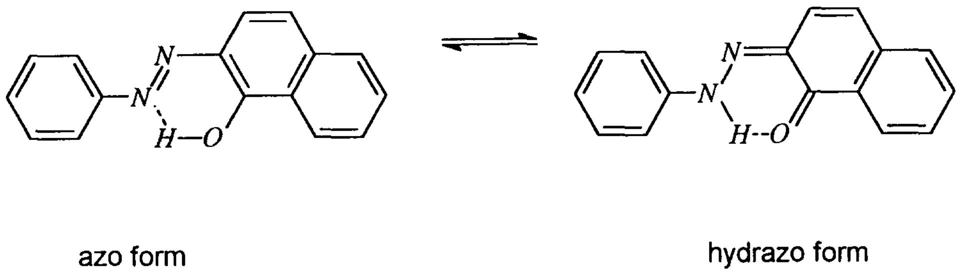
In the case of this study the azo (A)-quinonehydrazone (H) tautomerism in the following compounds, each of them the basis of many industrially important dyes



I. *1-Phenylazo-4-naphthol*



II. *1-Phenylazo-2-naphthol*



III. *2-Phenylazo-1-naphthol*

was investigated by using quantum-chemical calculations, and the results obtained were compared with our previous spectral investigations [2–6] in order to evaluate some relations between them, and attempt an explanation of this complex phenomenon in solution.

EXPERIMENTAL

The molecular structures of I-III were optimized at the AM1 [7], HF/3-21G and HF/6-31G** [8] levels. Semi-empirical AM1 molecular orbital calculations were performed with an MNDO93 program implemented in the Unichem 3.0 package (Cray Research Inc.). Ab-initio molecular orbital calculations were performed using Gaussian'94 [8].

The molecular orbital diagrams were drawn on a Silicon Graphics station using an AVS®Chemistry Viewer 1.5 (Molecular Simulations Inc.)

RESULTS AND DISCUSSION

The initial calculations of the structures of the tautomeric forms of I-III were carried out using the AM1 method. However, the resulting structure for the tautomeric forms of I were found to be nonplanar. In the A-form structure the phenyl ring was twisted by 19.5° to the N = N bond plane, whereas the naphthyl ring was twisted by −18°. In the H-form, the naphthyl ring was in an envelope conformation, totally out of planarity. These results were in disagreement with X-ray data [9] available for some derivatives of I, as well as the fact that the H-form shows fluorescence in solution [10]. The heats of formation obtained showed that in gas phase the A-form is more stable, in accordance with the experimental results for solution and gas phase [3, 11, 12]. Therefore, further calculations of I were performed with a basic structure which constrains all atoms to lie in the same plane. The resulting modified structures for I were found to be higher in energy only by 0.3 kcal mol^{-1} (0.04 kcal mol^{-1} and 0.28 kcal mol^{-1} for A and H-form, respectively) than those from the unconstrained structure optimization, keeping the general trend of the A-form as being more stable. It was also found that the trans-conformation of the phenyl and naphthyl rings is energetically preferred to the corresponding cis arrangement because of steric hindrance. In the case of II-III the planar state, was obtained without constraint, due to the intramolecular hydrogen bonding.

Since it is well known that in the case of azo compounds the ab-initio calculations give better results than AM1 calculations [13], the ab initio HF/3-21G method was then applied. The geometry in all cases was predicted correctly to be planar, but erroneously, the H-form was found to be the more stable. Therefore, using the optimized geometries from the HF/3-21G basis set as initial approximations, a further HF/6-31G** basis set was used for reoptimization. The stability of the optimized structures was proved by vibrational analysis [8].

In order to confirm the reliability of the results obtained, some selected bond lengths and angles of II (Fig. 1) are compared in Table 1 with the

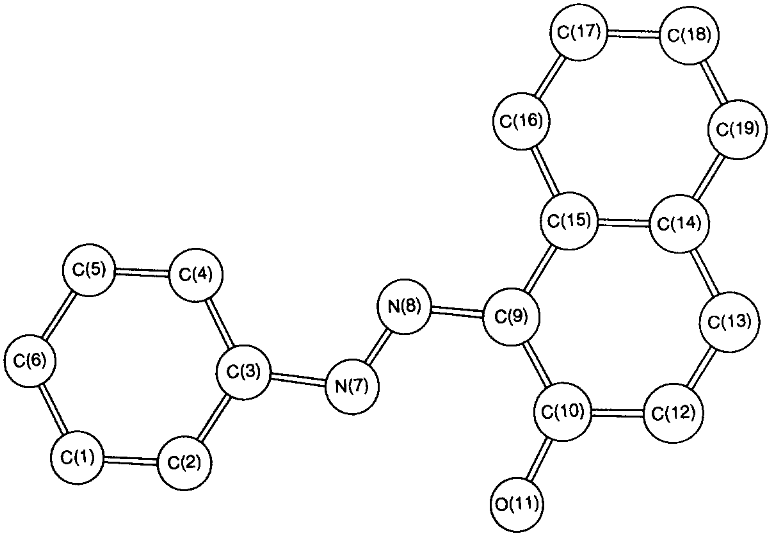


Fig. 1. Schematic presentation of II.

TABLE 1
Experimental and Calculated Bond Lengths (in angstroms), Angles (in degrees) and Dipole Moments (in debyes) for II

	AM1		*3-21G*		*6-31G***		*X-ray*	
	H	*A*	*H*	*A*	*H*	*A*	*[15]*	*[14]*[a]
C3-N7	1.423	1.434	1.397	1.424	1.398	1.420	1.415	1.406
N7-N8	1.297	1.233	1.326	1.248	1.297	1.226	1.314	1.308
N8-C9	1.333	1.424	1.291	1.403	1.286	1.403	1.340	1.338
C10-O11	1.247	1.366	1.235	1.347	1.212	1.327	1.267	1.261
C3-N7-N8	121.9	120.0	120.2	116.7	121.1	116.3	119.0	118.9
N7-N8-C9	124.5	121.0	122.8	118.9	123.3	118.3	118.5	118.4
N8-C9-C10	125.3	126.8	117.7	123.8	117.2	124.7	124.1	123.9
C9-C10-O11	121.9	126.6	121.7	123.5	122.0	124.3	121.7	121.3
μ	1.625	0.884	2.086	1.447	2.028	1.163		

[a] At 213 K.

existing experimental X-ray data [14, 15]. As can be seen from Table 1, the experimental bond lengths and angles lie between the calculated values for A- and H-form, which is in accordance with the fact that the tautomeric equilibrium exists even in the solid state [14]. It is worthwhile to note also that the data in Table 1 are in good agreement with statistically evaluated limits [16] for bond distances involved in the azo linkage (1.37 Å < R(C3-N7) < 1.49 Å; 1.20 Å < R(N7 = N8) < 1.28 Å) and in the hydrazo linkage (1.35 Å < R(C3-N7) < 1.47 Å; 1.30 Å < R(N7-N8) < 1.43 Å; 1.26 Å < R(N8 = C9) < 1.33 Å).

TABLE 2
Energies and Heats of Formation of the Tautomeric Forms of I-III

Dye	*AM1 ΔH (kcal mol^{-1})*			*HF/6-31G** E_{RHF} (a.u.)*			*K_T^{a}*	
	A	*H*	*H-A gap*	*A*	*H*	*H-A gap (kcal mol^{-1})*	*b*	*c*
I	76.18	84.69	8.51	−796.63223	−796.62979	1.531	0.24	0.11
II	76.06	79.01	2.95	−796.63823	−796.63779	0.276	0.72	0.49
III	75.26	77.46	2.20	−796.64064	−796.64153	−0.558	2.11	1.50

[a] Defined as ratio (H)/(A);
[b] in ethanol [2, 4–6];
[c] in i-octane [3–6].

The results for the energies of the tautomeric forms obtained, in comparison with the heats of formation from AM1, are presented in Table 2. The value for the A–H gap of I calculated with HF/6-31G** shows an excellent agreement with the experimental data available (0.84 kcal mol^{-1} in gas phase [12], 2 kcal mol^{-1} in methylcyclohexane [11, 17] and 2.5 kcal mol^{-1} in formamide [3]) which is a good confirmation of the reliability of the calculation results. The data for the A–H gaps in the dyes investigated show a change which is in accordance with the experimentally found tautomeric constants, and according to the HF/6-31G** method, the H-form in the case of III is more stable, which is likely to be consistent with the values for the K_T. The relationship between the calculated H–A gaps and K_T is shown in Fig. 2.

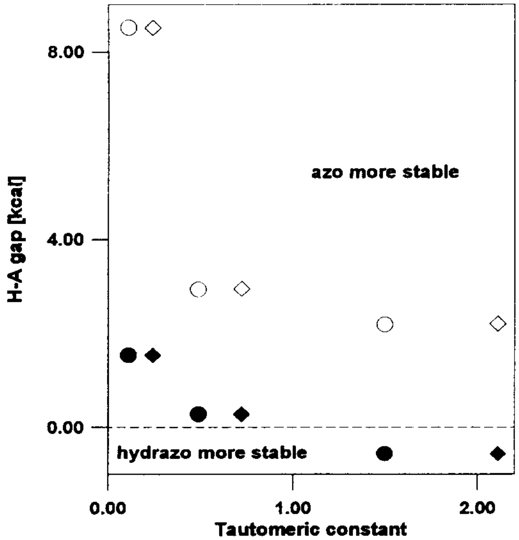
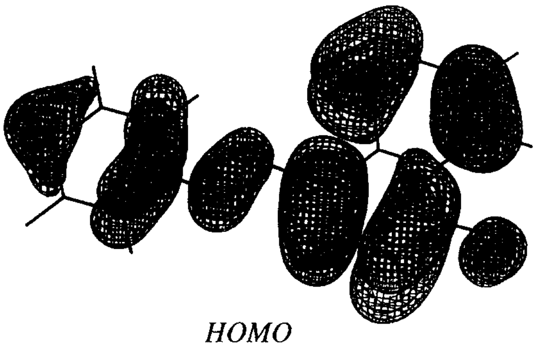
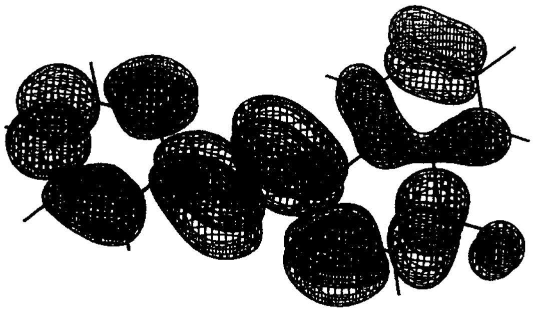


Fig. 2. Relation between the tautomeric constants in ethanol (◇) and i-octane (○) with the A–H gaps calculated by using AM1 (empty characters) and HF/6-31G** (filled characters) methods.

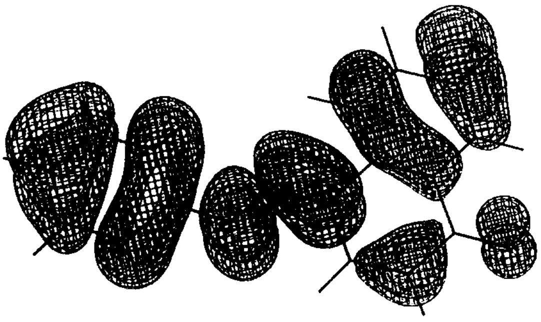


HOMO

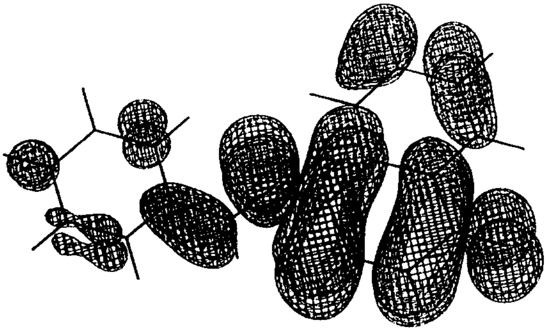


LUMO

Fig. 3. HOMO–LUMO molecular orbital diagrams of the A-form of I.



HOMO



LUMO

Fig. 4. HOMO–LUMO molecular orbital diagrams of the H-form of I.

Both A- and H-forms are typical donor-acceptor chromogens and the charge transfer of azo structure proceeds mainly from the OH group in the naphthyl ring towards the azo group, and to a smaller extent to the phenyl ring. This fact is well illustrated in Fig. 3, where the HOMO–LUMO molecular orbital diagrams for the A-form of I are presented.

The opposite is true for the hydrazone structure—the charge transfer proceeds mainly from the phenyl ring and the aniline-like N-atom towards the carbonyl group in the naphthyl ring and the quinoneimine N-atom (Fig. 4).

This fact indicates the opposite effect of substituents on the stability of A- (stabilized by donors) and H-form (stabilized by acceptors), especially in the para-position [3, 4], but it is difficult to make such a clear conclusion for the meta-substituents.

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