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## SUBSTITUENT AND SOLVENT EFFECTS ON THE TAUTOMERISM OF 1-PHENYLAZO-2-NAPHTHOL: A COMPUTATIONAL STUDY

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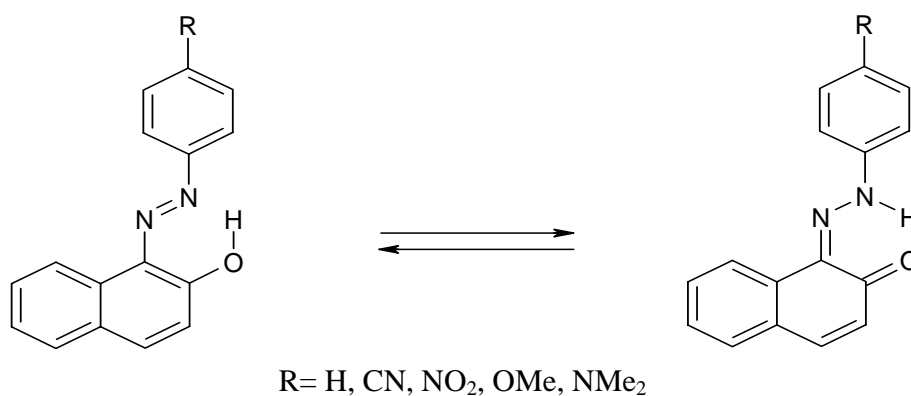
### Abstract

The tautomerism between enol and inone forms of 1-phenylazo-2-naphthol is discussed in this work. The density functional theory (DFT) method is used at the level of B3LYP/6-31+G(d,p) for computations and it showed good agreement with the experimental data qualitatively. Generally quinone forms (of studied compounds) are more stable than naphthol forms. Electron attracting groups move the equilibrium also towards quinone form while releasing groups move the equilibrium to the naphthol form. The polarity of solvents does not have significant effect on the equilibrium.

### Introduction

Intramolecular proton transfer in the ground and/or excited state of Schiff bases has important consequences on their electronic structure which can be exploited for their thermochromic and/or photochromic behavior,<sup>1,2</sup> the design of molecular electronic devices,<sup>3</sup> as well as their suitability as agents in photodynamic cancer therapy.<sup>4</sup> Furthermore, intramolecular hydrogen bonding in 1,3-diketones,  $\beta$ -enaminones or ketohydrazones<sup>5-7</sup> and related heterodienes<sup>8</sup> is of fundamental importance in the theory of hydrogen-bonding.<sup>9-11</sup> Closely related to this enol-imine – keto-amine tautomerism of Schiff bases with similar practical consequences is the azo–hydrazo tautomerism in the analogous arylazo phenol derivatives.<sup>12</sup> In continuation of our previous work on the azo –

hydrazo and/or enol-imine keto-amine tautomerism in phenylazonaphthols and naphthaldehyde Schiff bases,<sup>13</sup> here we present the results of a computational study concerning the substituent effects (structural influence) and environment (solvents effects) on the tautomeric equilibria of 1-(4-R-phenylazo)-2-naphthol by density functional theory calculations. Computed data will be compared with available experimental data.



**Figure 1**

The main emphasis of this work is to assess the influence on the tautomeric equilibrium of the nature of substituents (both electron donors and acceptors) as well as the polarity and the hydrogen bond accepting/donating ability of the solvents (**CH<sub>3</sub>CN**, **CH<sub>3</sub>OH**, **CHCl<sub>3</sub>**, and **CCl<sub>4</sub>**). The substituents chosen are shown in Figure 1.

### Computational details

The program Gaussian 03 has been employed for all computations.<sup>14</sup> (evaluation of geometries and energies)

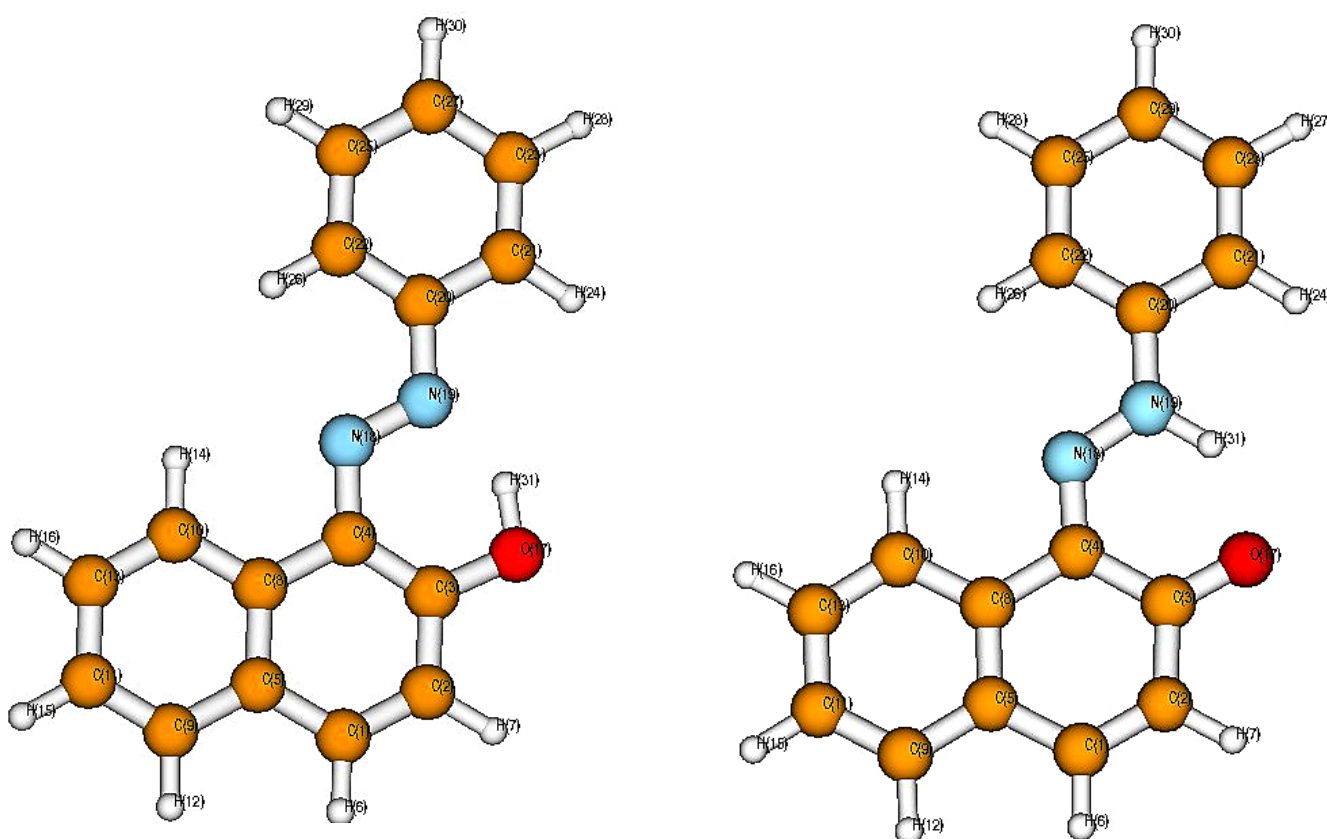
Geometries were fully optimized at the B3LYP 6-31+G(d,p) level of theory.<sup>15</sup> Solvent effects (**CH<sub>3</sub>CN**, **CH<sub>3</sub>OH**, **CHCl<sub>3</sub>**, and **CCl<sub>4</sub>**) were estimated by B3LYP 6-31+G(d,p) optimization using the Integral Equation Formalism of the Polarized Continuum Model (IEF-PCM).<sup>16</sup>

All structures were characterized as true minima frequency calculations. Thermodynamic quantities were obtained through standard harmonic oscillator-rigid rotator treatments.

## Results and Discussion

### Structures

The lowest energy structures for both tautomers of the unsubstituted parent compound, obtained by B3LYP/6-31+G(d,p) calculations, are shown in Figure 2.



**Figure 2** Calculated (B3LYP/6-31+G(d,p)) lowest energy structures of azo and hydrazo tautomers of 1-phenylazo-2-naphthol

The values of some selected bond distances, bond angles and dihedral angles (geometric data) of 1-(4-dimethylaminophenylazo)-2-naphthol (experimental from CCDC<sup>17</sup> and computed) are presented in Table A.

**Table A: Experimental & computed bond lengths (in angstroms), bond angles & torsion angles (in degrees)**

<b>Bond Length</b>	<b>Exp.</b>	<b>Calc.</b>	<b>Bond Angle</b>	<b>Exp.</b>	<b>Calc.</b>	<b>Torsion Angle</b>	<b>Exp.</b>	<b>Calc.</b>
C <sub>4</sub> -N <sub>18</sub>	1.392	1.389	C <sub>3</sub> -O <sub>17</sub> -H <sub>31</sub>	103.81	105.87	C <sub>4</sub> -N <sub>18</sub> -N <sub>19</sub> -C <sub>20</sub>	179.7	-179.9
N <sub>18</sub> -N <sub>19</sub>	1.286	1.278	C <sub>4</sub> -C <sub>3</sub> -O <sub>17</sub>	122.13	121.98	C <sub>3</sub> -C <sub>4</sub> -N <sub>18</sub> -N <sub>19</sub>	-0.9	0.2
C <sub>3</sub> -O <sub>17</sub>	1.337	1.340	N <sub>18</sub> -C <sub>4</sub> -C <sub>3</sub>	125.17	124.05	N <sub>18</sub> -C <sub>4</sub> -C <sub>3</sub> -O <sub>17</sub>	-1.1	-0.1
O <sub>17</sub> -H <sub>31</sub>	1.002	1.006	N <sub>19</sub> -N <sub>18</sub> -C <sub>4</sub>	114.71	116.76	C <sub>4</sub> -C <sub>3</sub> -O <sub>17</sub> -H <sub>31</sub>	0.4	-0.0
N <sub>19</sub> -H <sub>31</sub>	1.614	1.647	N <sub>18</sub> -N <sub>19</sub> -C <sub>20</sub>	116.88	116.92	N <sub>18</sub> -N <sub>19</sub> -C <sub>20</sub> -C <sub>21</sub>	-177.1	-179.7

The experimental values are approximately equal to the computed data, hence the comparison of computed data with experimental show the reliability of results.

### Relative energies

The computed relative Gibbs free energies of phenol (azo) and quinone (hydrazo) forms,

$$\Delta G_{rel} = \Delta G(\text{azo}) - \Delta G(\text{hydrazo})$$

are presented in Table B.

**Table B: Computed relative Gibbs free energies (kcal mol<sup>-1</sup>)**

<b>Compounds</b>	<b>Gas phase</b>	<b>CH<sub>3</sub>CN</b>	<b>CH<sub>3</sub>OH</b>	<b>CHCl<sub>3</sub></b>	<b>CCl<sub>4</sub></b>
	NMe <sub>2</sub>	-1.17	0.49	0.43	-0.03
OCH <sub>3</sub>	0.05	1.63	1.64	1.12	0.65
H	0.94	2.42	2.45	1.95	1.51
CN	1.28	2.91	2.92	2.32	1.96
NO <sub>2</sub>	1.49	3.44	3.48	2.80	2.29

According to the calculated Gibbs free energies electron attracting substituents should shift the equilibrium towards the quinone form ( $\Delta G_{rel} > 0$ ), while electron

donating substituents preferentially stabilize the phenol tautomer ( $\Delta G_{rel} < \Delta G_{rel} (R = H)$ ). Irrespective of the nature of the substituents, polar solvents shift the azo–hydrazo tautomeric equilibrium towards the hydrazo (quinone) form.

The experimental tautomerization constants  $K_T$ , defined by

$$K_T = [\text{hydrazo}]/[\text{azo}]$$

of 1-phenylazo-2-naphthol and its derivatives, obtained via  $^{13}\text{C}$  NMR<sup>18</sup> measurements, are presented in Table C.

**Table C: The experimental  $K_T$  values**

Compounds	$\text{CD}_3\text{CN}$	$\text{CDCl}_3$	$\text{CCl}_4$
H	2.188	2.587	1.692
$\text{NO}_2$	a	a	19.755
OEt	0.813	0.734	0.49
$\text{NMe}_2$	0.236	0.382	0.248

“a” only quinone form detectable

Experimental tautomerization constants  $K_T$  are qualitatively in line with the computed  $\Delta G_{rel}$  –values: increase of hydrazo tautomer in more polar solvents, e.g.  $K_T$  in  $\text{CCl}_4$  vs.  $K_T$  in  $\text{CD}_3\text{CN}$  for  $R = \text{H}$ ,  $\text{NO}_2$ , and OEt; shift of the tautomeric equilibrium towards azo and hydrazo forms by electron donating ( $R = \text{OEt}$ ,  $\text{NMe}_2$ ) and electron withdrawing substituents ( $R = \text{NO}_2$ ), respectively.

So far,  $K_T$  – values determined by U/Vis spectroscopy are available only for the unsubstituted derivative.<sup>19</sup> They differ substantially from those determined by NMR:  $K_T = 0.66$  ( $\text{CH}_3\text{CN}$ ), 1.463 ( $\text{CHCl}_3$ ), 0.56 ( $\text{CCl}_4$ ), and 1.551 ( $\text{CH}_3\text{OH}$ ); a more recent value in  $\text{CH}_3\text{OH}$  is obtained as  $K_T = 0.83$ .

### Atoms-in-Molecules (AIM) analysis<sup>20</sup>

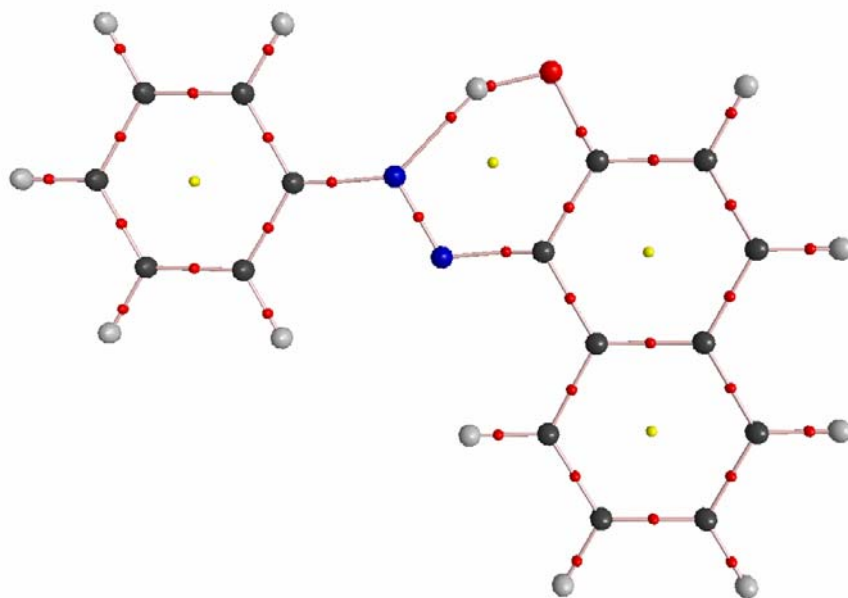
Since intramolecular hydrogen-bonding is a prominent feature in o-hydroxy azo benzenes and the analogous Schiff bases, we have analyzed the strength of this intramolecular hydrogen bonding by means of the atoms-in-molecule procedure.

Relevant data (electron density at bond critical points,  $\rho_{\text{BCP}}$ , and the respective Laplacians,  $\nabla^2\rho_{\text{BCP}}$ ) are given in Table X. In general, the greater the value of electron density at a certain bond critical point (BCP),  $\rho_{\text{BCP}}$ , the stronger is interaction between two atoms forming this bond, no matter what kind of interaction (bond) it is. In the case of covalent bonds the Laplacian,  $\nabla^2\rho_{\text{BCP}}$ , adopts negative values, while positive values of  $\nabla^2\rho_{\text{BCP}}$  characterize closed shell interaction.

An analysis of the electron density measured at H-bond BCPs suggests that O-H...N bond is relatively stronger than N-H...O.

**Table D Results of the AIM analysis for the unsubstituted derivative (R = H) in CH<sub>3</sub>OH.**

bond	O-H (N-H)		H...N (H...O)	
	$\rho_{\text{BCP}}$	$\nabla^2\rho_{\text{BCP}}$	$\rho_{\text{BCP}}$	$\nabla^2\rho_{\text{BCP}}$
Azo-tautomer	0.3108	-1.6780	0.0655	0.1284
Hydrazo-tautomer	0.3236	-1.7488	0.0460	0.1418



**Figure 3.** Molecular graph of the system under discussion; big circles correspond to attractors, small ones to the bond critical points (BCPs, red colour) and the ring critical

points (RCPs, yellow colour). Tautomeric form with O-H...N hydrogen bond has been selected. Bond path with corresponding BCP can be observed for H...N interaction.

## Conclusion

The relative energy values of all studied compounds show that electron attracting substituents leads the equilibrium towards quinone form and vice versa. The polarity of the solvent also has a little effect on the stability and decreasing in the polarity shifts the equilibrium towards phenolic form. It can be concluded from the results that greater stability of quinoid form in polar solvents is due to stronger H-bonding between the oxygen and the hydrogen of polar solvents.

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## References

- 1 Reviews: (a) Hadjoudis, E. *Mol. Eng.* **1995**, *5*, 301-337; (b) Hadjoudis, E. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 127-134.
- 2 (a) Hadjoudis, E.; Moustakali-Mavridis, I. *Mol. Cryst. Liq. Cryst.* **1990**, *186*, 31-36; (b) Hadjoudis, E.; Mavridis, I. M.; Dziembowska, T.; Rozwadowski, Z.; Anulewicz, R. *Mol. Eng.* **1999**, *8*, 97-104; (c) Milia, F.; Hadjoudis, E.; Seliger, J. *J. Mol. Struct.* **1988**, *177*, 191-197; (d) Hadjoudis, E.; Argyroglou, J.; Moustakali-Mavridis, I. *Mol. Cryst. Liq. Cryst.* **1988**, *156*, 39-48; (e) Hadjoudis, E.; Vittorakis, M.; Moustakali-Mavridis, I. *Tetrahedron* **1987**, *43*, 1345-1360; (f) Hadjoudis, E.; Rontoyianni, A.; Ambroziak, K.; Dziembowska, T.; Mavridis, I. M. *J. Photochem. Photobiol. A* **2004**, *162*, 521-530.
- 3 (a) Zhang, Y.; Lu, Z. H. *Mat. Chem. Phys.* **2000**, *63*, 188-195; (b) Zhang, Y.; Lu, Z.-H. *Mat. Chem. Phys.* **1999**, *57*, 253-259.
- 4 Isak, S. J.; Eyring, E. M.; Spikes, J. D.; Meekins, P. A. *J. Photochem. Photobiol. A* **2000**, *134*, 77-85.
- 5 (a) Bertolasi, V.; Ferretti, V.; Gilli, P.; Yao, X.; Li, C.J. *New J. Chem.* **2008**, *32*, 694-704; (b) Gilli, P.; Bertolasi, V.; Pretto, L.; Lycka, A.; Gilli, G. *J. Am. Chem. Soc.* **2002**, *124*, 13554-13567; (c) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2000**, *122*, 10405-10417; (d) Gilli, P.; Bertolasi, V.; Pretto, L.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **2004**, *126*, 3845-3855; (e) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G.; Vaughan, K. *New J. Chem.* **1999**, *23*, 1261-1267; (f) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Chem. Soc., Perkin Trans. 2* **1997**, 945-952; (g) Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *Acta Crystallogr. Sect. B-Struct. Sci* **1994**, *B50*, 617-625; (h) Bertolasi, V.; Nanni, L.; Gilli, P.; Ferretti, V.; Gilli, G.; Issa, Y. M.;



- Sherif, O. E. *New J. Chem.* **1994**, *18*, 251-261; (i) Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023-1028.
- 6 (a) Rybarczyk-Pirek, A. J.; Grabowski, S. J.; Malecka, M.; Nawrot-Modranka, J. *J. Phys. Chem. A* **2002**, *106*, 11956-11962; (b) Malecka, M.; Grabowski, S. J.; Budzisz, E. *Chem. Phys.* **2004**, *297*, 235-244; (c) Bouchy, A.; Rinaldi, D.; Rivail, J.-L. *Int. J. Quant. Chem.* **2004**, *96*, 273-281.
- 7 (a) Buemi, G.; Zuccarello, F.; Venuvanalingam, P.; Ramalingam, M. *Theor. Chem. Acc.* **2000**, *104*, 226-234; (b) Buemi, G. *J. Mol. Struct. (THEOCHEM)* **2000**, *499*, 21-34; (c) Buemi, G.; Zuccarello, F. *J. Mol. Struct. (THEOCHEM)* **2002**, *581*, 71-85.
- 8 (a) Lammertsma, K.; Bharatam, P. V. *J. Org. Chem.* **2000**, *65*, 4662-4670; (b) Long, J. A.; Harris, N. J.; Lammertsma, K. *J. Org. Chem.* **2001**, *66*, 6762-6767.
- 9 (a) Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1-15; (b) Gilli, P.; Ferretti, V.; Bertolasi, V.; Gilli, G. *Adv. Mol. Struct. Res.* **1996**, *2*, 67-102; (c) Gilli, P.; Bertolasi, V.; Pretto, L.; Antonov, L.; Gilli, G. *J. Am. Chem. Soc.* **2005**, *127*, 4943-4953.
- 10 (a) Grabowski, S. J. *J. Phys. Org. Chem.* **2004**, *17*, 18-31; (b) Grabowski, S. J. *J. Phys. Org. Chem.* **2003**, *16*, 797-802; (c) Grabowski, S. J. *J. Phys. Chem. A* **2001**, *105*, 10739-10746.
- 11 (a) Scheiner, Steve *Hydrogen Bonding: A Theoretical Perspective*, Oxford University Press, New York, N. Y., 1997; (b) Perrin, C. L.; Ohta, B. K. *Bioorg. Chem.* **2002**, *30*, 3-15; (c) Godzisz, D.; Ilczyszyn, M. M.; Ilczyszyn, M. F. *J. Mol. Struct.* **2002**, *606*, 123-137; (d) Frey, P. A. *Magn. Reson. Chem.* **2001**, *39*, S190-S198.
- 12 Reviews: (a) Mustroph, H. *Z. Chem.* **1987**, *27*, 281-289; (b) Whitaker, A. *J. Soc. Dyers Colour.* **1995**, *111*, 66-72; (c) Whitaker, A. *J. Soc. Dyers Colour.* **1978**, *94*, 431-435; (d) Ball, P.; Nicholls, C. H. *Dyes Pigm.* **1982**, *3*, 5-26.
- 13 Fabian, M.F.; Antonov, L.; Nedeltcheva, D.; Kamounah, F.S.; Taylor, P.J. *J. Phys. Chem. A* **2004**, *108*, 7603-7612.
- 14 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.04*, Gaussian, Inc., Wallingford CT, 2004
- 15 (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652; (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B*, **1988**, *37*, 785-789. (c) Hariharan, P.C.; Pople, J.A. *Theoret. Chim. Acta* **1973**, *28*, 213-222; (d) Clark, T.; Chandrasekhar, T.; v.Rague Schleyer, P. *J. Comp. Chem.* **1983**, *4*, 294-301.
- 16 Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (Theochem)* **1999**, *464*, 211-226.
- 17 Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187-204.
- 18 Alarcon, S.H.; Olivieria, A.C.; Sanzb, D.; Claramunt, R.M.; Elguero, J. *J. Mol. Struct.* **2004**, *705*, 1-9.
- 19 Antonov, L.; Stoyanov, S.; Stoyanova, T. *Dyes Pigm.* **1995**, *27*, 133-142.
- 20 Bader, R.F.W.; *Atoms in Molecules: A Quantum Theory*; Clarendon Press, Oxford, 1990.