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# Water-assisted Ground State Intra-molecular Proton Transfer in 2,5-dihydroxy-Substituted Azobenzenes: Experimental and Computational Studies

Dhiraj Das<sup>a</sup> and Angshuman RoyChoudhury\*a

The phenomenon of ground-state proton transfer in a series of2,5-dihydroxy azobenzenes derivatives has been studied. The mechanism for proton transfer in dimethylacetamide (DMA)-water mixture has been investigated by UV-Vis Spectroscopy. The Time-Dependent Density Functional Theory (TD-DFT) calculation was performed to get further confirmation. The intramolecular hydrogen bond between the hydrogen of the *o*-hydroxy group and azo-group is found to be reinforced in the hydrogen transfer process. The topological properties of the intramolecular interactions have been determined by atoms in molecules (AIM) calculations with the help of AIM2000 package. It has been observed that water and substitutions in the *ortho*-position corresponding to azo-group has facilitated the proton transfer mechanism to occur in the ground state. The effect of substitutions and water molecule has been investigated by DFT calculations.

## Introduction

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Functionalized azobenzenes(ABs) represent an important class of compounds mainly because of their photo-switching properties and therefore they are used as molecular devices.<sup>1-3</sup> A prominent feature of hydroxy-azobenzenes (OH-ABs) is keto/enol tautomerism (Scheme 1). This tautomerism has been exploited towards signalling and switching.<sup>4</sup>Hydroxy group, close to the azo group (-N=N-), shows hydrogen atom-coupled electron transfer (PCET) as well.<sup>5,6</sup>PCET reactions have importance in many biological processes and small molecule activations related to the conversion and storage of solar energy, mainly carbon dioxide reduction and water oxidation.7-10 Further, the OH-ABs exhibits ground/excited state proton transfer through hydrogen bonding. Intra-molecular and intermolecular proton transfer have gained great interest in chemistry, physics, and biology due to their application as fluorescence chemo-sensors, laser-dyes, and molecular-switches.<sup>11-</sup> <sup>14</sup> The hydrogen bonding interactions with the solvent molecules play important role in this proton transfer reaction. Many groups have studied proton transfer mechanism spectroscopically and by theoretical calculations.<sup>15-20</sup> They suggested that hydrogen bonding and water molecules assist these proton transfers in the excited state or ground state. Wachtveitl et al. have studied proton transfer mechanism on OH-ABs in water by ultrafast spectroscopic studies

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and theoretical calculations (DFT).<sup>21</sup> Ozen*et al.* have studied the effect of cooperative hydrogen bonding in keto/enol tautomerism of hydroxyl-azo dyes by theoretical calculations (DFT).<sup>22</sup>

Herein, we have synthesized four derivatives of dihydroxyazobenzene (1-4) (Scheme 2) and studied intramolecular proton transfer in the ground state. We have structurally characterized the intermediate for enol/keto tautomerism for the first time. Three keto forms among four compounds have been structurally characterized along with enol forms. Many groups have suggested that water molecules and hydrogen bonding are the initiators for the proton transfer. We have validated such explanations by structural chemistry and computations.



Scheme 1 Keto/enol tautomerism in OH-ABs.



**Scheme 2** (a) Dihydroxy azo-benzene derivatives and (b) keto/enol tautomerism.

#### Experimental section Starting Materials

All the compounds were purchased from various commercial suppliers and were used as received. Solvents and reagents were purchased from Merck chemicals, India, Sigma-Aldrich and used as received.

<sup>&</sup>lt;sup>a.</sup> Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali, Sector 81, S. A. S. Nagar, Manuali PO, Mohali, 140306, Punjab, India. E-mail: <u>angshurc@lisermohali.ac.in;</u> Fax: +911722293167

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 Table 1.Crystallographic and Refinement Data of all the compounds.

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Compound ID	1k	2e	Зе	3k	4k	2-int
CCDC number	1876826	1876827	1876822	1876823	1876825	1876824
Formula	$C_{12}H_9N_3O_4$	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub>	C <sub>16</sub> H <sub>18</sub> CIN <sub>3</sub> O <sub>3</sub>	C <sub>12</sub> H <sub>11</sub> CIN <sub>2</sub> O <sub>3</sub>	$C_{12}H_{11}BrN_2O_3$	$C_{13}H_9N_3O_2$
Formula weight	259.22	312.33	336.06	266.68	311.14	239.23
Crystal size (mm)	0.42×0.41× 0.4	0.52×0.4× 0.22	0.34×0.32× 0.28	0.30×0.26×0.20	0.2×0.15×0.12	0.32×0.12×0.09
Crystal system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P21/n	рĪ	р <u>1</u>	P21/n	P2 <sub>1</sub> /n	P21/c
<i>a,</i> Å	11.8236(6)	7.0323(3)	7.0839(3)	3.9592(2)	3.93930(10)	10.0695(11)
<i>b,</i> Å	8.6618(3)	8.6204(4)	10.8648(6)	13.8353(7)	13.8586(4)	4.4780(5)
<i>c,</i> Å	12.0259(6)	13.7182(6)	10.9553(6)	22.1033(11)	21.9545(7)	23.887(3)
α (°)	90	105.738(2)	90.615(5)	90	90	90
β (°)	113.493(6)	94.770(2)	94.232(4)	93.241(5)	93.737(3)	92.333(3)
γ (°)	90	103.820(2)	107.982(5)	90	90	90
<i>V</i> , Å <sup>3</sup>	1129.53(10)	767.47(6)	799.30(7)	1208.81(11)	1196.02(6)	1076.2(2)
Z	4	2	2	4	4	4
Ζ'	1	1	1	1	1	1
$ ho_{calc}$ (g cm <sup>-3</sup> )	1.524	1.352	1.396	1.465	1.728	1.476
μ (mm <sup>-1</sup> )	0.118	0.096	0.258	0.318	3.439	0.104
Temperature (K)	100.0(2)	100.0(2)	100.0(2)	298.0(2)	100.0(2)	100.0(2)
2Θ <sub>min, max</sub>	5.98-49.97	3.124-49.994	5.332-49.982	5.89-49.994	5.88-49.988	4.048-53.044
F (000)	536.0	328.0	352.0	552.0	624.0	496.0
No. of Reflections collected	6344	10582	9552	7717	8806	15398
R <sub>int</sub>	0.0166	0.0167	0.0242	0.0428	0.0341	0.0489
No. of unique reflections	1984	2711	2799	2131	2110	2226
Data/restraints/param eters	1984/0/180	2711/0/218	2799/0/219	2131/0/179	2110/0/179	2226/0/171
Diffractometer and Detector	Rigaku XtaLAB mini and Mercury375/M CCD	Bruker Kappa Apex II and CCD	Rigaku XtaLAB mini and Mercury375/M CCD	Rigaku XtaLAB mini and Mercury375/M CCD	Rigaku XtaLAB mini and Mercury375/M CCD	Bruker Venture a Photon 100 CM
$R_1[I>2\sigma(I)]$	0.0363	0.0324	0.0487	0.0580	0.0309	0.0510
wR2(all data)	0.0983	0.1020	0.1365	0.1889	0.0761	0.1544
GooF on F <sup>2</sup>	1.077	1.099	1.098	1.027	1.102	1.087
Largest diff. Peak/hole/e (ų)	0.20/-0.23	0.23/-0.23	0.53/-0.25	0.54/-0.23	0.81/-0.37	0.22/-0.29
Index ranges	$-12 \le h \le 14$	-8 ≤ h ≤ 8	-8 ≤ h ≤ 8	$-4 \le h \le 4$	$-4 \le h \le 4$	-12 ≤ h ≤ 12
	$-10 \le k \le 10$	-8 ≤ k ≤ 10	-12 ≤ k ≤ 12	-16 ≤ k ≤ 16	-16 ≤ k ≤ 16	-5 ≤ k ≤ 5
	$-14 \leq l \leq 14$	-16 < 1 < 16	-13 <   < 13	-26 < 1 < 24	-26 < 1 < 21	-29 < 1 < 29

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#### Table 2 Bond distances

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	Bond	Distances (Å)		Bond	Distances (Å)
1k	C7-N2	1.3979(18)		N1-N2	1.281(2)
	N2-N1	1.3189(16)		N1-C6	1.390(3)
	N1-C1	1.3254(18)	Зе	C6-C1	1.433(3)
	C1–C6	1.472(2)		C101	1.351(3)
	C6-01	1.2788(16)			
	N1-N2	1.2752(15)		N1-N2	1.306(3)
2e	N2-C8	1.3898(16)		N2-C7	1.341(3)
	C8–C9	1.4274(17)	SK	C7–C8	1.456(4)
	C9-01	1.3481(16)		C8–O2	1.292(3)
2-int	N1-N2	1.279(2)		N1-N2	1.301(3)
	N1-C1	1.393(3)	al.	N2-C7	1.344(4)
	C1–C6	1.427(3)	44	C7–C8	1.459(4)
	C6-01	1.344(3)		C8–O2	1.298(4)

## Table 3. Hydrogen bond distances of all the compounds

	Donor (D)-HAcceptor(A)	D-H (Å)	HA (Å)	DA (Å)	∠D-HA (°)	Symmetry
	02–H2…O1	0.95(2)	1.64(2)	2.5837(16)	176.2(18)	1/2 -X,Y-1/2,1/2 -Z
1k	N2–H2A…O1	0.92(2)	1.85(2)	2.5802(16)	135.3(15)	Intramolecular
	N2–H2A…O3	0.92(2)	2.033(18)	2.6288(16)	121.(16)	Intramolecular
	01-H1…N1	0.87(2)	1.81(2)	2.5860(13)	149(2)	intramolecular
	01–H1…N2	0.87(2)	2.44(2)	2.9514(14)	118(2)	Intramolecular
2e	02–H2…O3	0.92(3)	1.68(3)	2.5809(14)	165.9(17)	Intramolecular
	C3–H3…N3	0.95	2.58	3.4743(18)	157	-x,-y,1-z
	C5–H5…O3	0.95	2.54	3.4833(15)	175	1-x,2-y,1-z
	C10-H10O2	0.95	2.59	3.4885(15)	$\angle$ D-H.A (°)       Symmetry         16)       176.2(18) $\frac{1}{2}$ -x, y- $\frac{1}{2}$ , $\frac{1}{2}$ 16)       135.3(15)       Intramolecu         16)       121.(16)       Intramolecu         13)       149(2)       intramolecu         14)       118(2)       Intramolecu         14)       165.9(17)       Intramolecu         14)       165.9(17)       Intramolecu         14)       165.9(17)       Intramolecu         (18)       157       -x,-y,1-z         (15)       175       1-x,2-y,1-z         (15)       158       1-x,1-y,-z         114(2)       Intramolecu         2)       146(3)       Intramolecu         2)       146(3)       Intramolecu         3)       167(3)       1-x,-y,1-z         4)       150       1-x,-y,1-z         5)       150       1-x,-y,1-z         6)       139       1+x,2+y,z         1117(3)       Intramolecu       148(3)         1177(5)       Intermolecu       15         128       Intermolecu       168(4)         132(3)       Intramolecu       163         163(5)       1+x,y,z </td <td>1-<i>x</i>,1-<i>y</i>,-<i>z</i></td>	1- <i>x</i> ,1- <i>y</i> ,- <i>z</i>
2-int	01–H1…N1	1.14(3)	2.28(3)	2.929(2)	114(2)	Intramolecular
	01–H1…N2	1.14(3)	1.52(3)	2.541(2)	146(3)	Intramolecular
	O2–H2…N3	0.92(3)	2.00(3)	2.900(3)	167(3)	1- <i>x</i> ,- <i>y</i> ,1- <i>z</i>
	C5–H5…O1	0.95	2.39	3.251(3)	150	1-x,-y,1-z
	C10-H10O2	0.95	2.51	3.286(3)	139	1+ <i>x</i> ,2+ <i>y</i> , <i>z</i>
	01–H1…N1	0.91(3)	2.40(4)	2.933(2)	117(3)	Intramolecular
_	01–H1…N2	0.91(3)	1.74(3)	2.555(2)	148(3)	Intramolecular
3e	02–H2…O3	0.78(3)	1.84(4)	2.619(2)	177(5)	Intermolecular
	C2–H2A…O3	0.93	2.53	3.183(2)	2.D-HA()       Symmetric         5)       176.2(18) $\frac{1}{2}$ -x, y- $\frac{1}{2}$ 5)       135.3(15)       Intramo         5)       121.(16)       Intramo         5)       121.(16)       Intramo         5)       121.(16)       Intramo         6)       149(2)       intramo         118(2)       Intramo         3)       157       -x,-y,1-z         5)       175       1-x,2-y,1         5)       158       1-x,1-y,-         114(2)       Intramo       146(3)         167(3)       1-x,-y,1-       150         150       1-x,-y,1-       150         167(3)       1-x,-y,1-       139         148(3)       Intramo       148(3)         177(5)       Intermo       168(4)         177(5)       Intermo       168(4)         132(3)       Intramo       168(4)         132(3)       Intramo       163(	Intermolecular
	01–H1…O3	0.94(4)	1.69(4)	2.614(3)	168(4)	1-x,1-y,1-z
	N1–H(1A)…Cl1	1.02(4)	2.46(4)	2.941(2)	109(3)	Intramolecular
3k	N1–H(1A)…O2	1.02(4)	1.75(4)	2.539(3)	132(3)	Intramolecular
	O3–H(3A)…O2	0.90(4)	1.94(4)	2.826(3)	168(4)	Intramolecular
	O3–H(3B)…O2	0.99(6)	1.82(5)	2.773(3)	163(5)	1+ <i>x</i> , <i>y</i> , <i>z</i>
	N1-H(1A)···Br1	0.77(4)	2.68(3)	3.064(2)	113(3)	Intramolecular
	N1-H(1A)···O2	0.77(4)	1.90(4)	2.551(3)	142(3)	Intramolecular
4k	01–H1…O3	0.86(4)	1.74(4)	2.603(3)	175(4)	1-x,1-y,1-z
	O3–H(3A)…O2	0.91(5)	1.86(5)	2.743(3)	165(5)	-1+ <i>x</i> , <i>y</i> , <i>z</i>
	O3–H(3B)…O2	0.91(4)	1.93(4)	2.816(3)	165(4)	intramolecular

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#### Synthesis and Characterization

Since the method of the synthesis of all the compounds is the same, only a representative procedure is described below.

All the compounds were synthesized using the procedure reported in the literature.<sup>23</sup>An ice-cooled solution of sodium nitrite (NaNO<sub>2</sub>, 4.1 mmol) in water was added to the solution of amine(4 mmol) in dilute hydrochloric acid (6N, 8 mL) at 0-5 °C and then the mixture was stirred for half an hour. After that this cooled diazonium salt solution was added to the solution of resorcinol (4 mmol), sodium hydroxide (NaOH, 12 mmol) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 12 mmol) in water at 0-5 °C. Then mixtures were stirred for 1 hour at 0-5 °C. After that, the mixtures were filtered and then the residues were washed with water and dissolved in different solvents for crystallization.

#### Crystallization

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All are the compounds were recrystallized using different solvents. Suitable single crystals for X-ray diffraction were obtained from ethanol (EtOH), dimethylformamide (DMF), dimethylacetamide (DMA) and tetrahydrofuran (THF)-methanol (MeOH) mixture for the compound  $1{(E)-4-((2-nitrophenyl)diazenyl)benzene-1,3-diol}, 2{(E)-2-((2,4-dihydroxyphenyl)diazenyl)benzonitrile},3{(E)-4-((2-nitrophenyl)diazenyl)benzonitrile},3{(E)-4-((2-nitrophenyl)diazenyl)benzene-1,3-diol})$ 

chlorophenyl)diazenyl)benzene-1,3-diol}, and  $4\{(E)-4-((2-bromophenyl)diazenyl)benzene-1,3-diol\}, respectively. Suitable single crystals for X-ray diffraction were also obtained from THF-MeOH mixture in case of$ **3**. The asymmetric unit of all the compounds contains one molecule of the azo-compound. Their crystallographic parameters are represented in Table 1. All the aromatic hydrogen atoms were fixed at their geometrically ideal locations and refined using riding model but the H atoms linked to O or N atoms were located from the difference Fourier map and were refined isotropically.

#### **Computational Details**

All the theoretical calculations have been done using Gaussian 09<sup>24</sup> program and Gauss View 0525 has been used as a graphical interface. The interaction energy calculations were performed at Møller-Plesset perturbation theory (MP2) level using 6-31G(d) basis set, diffuse and polarization functions were used for halogens. For Topological parameter calculations, the suitable wavefunction files were generated using Gaussian 09 and those wavefunction files were used as input for AIM2000 package<sup>26</sup> for analysis of topological parameters like electron densities ( $\rho_c$ ) and Laplacian ( $\nabla$  $^{2}\rho_{c}$ ) of electron density at bond critical point (BCPs) and ring critical point (RCPs). For Time-Dependent Density Functional Theory (TD-DFT) calculations, all the geometries were optimized at MP2 level in gas phase then single point energy calculations have been done at DFT/B3LYP level using 6-311G(2d,p) as a basis set and diffuse and polarization functions were used for halogens. The effect of the solvents were modelled with the polarizable continuum model (PCM).<sup>27</sup> Density Functional Theory (DFT) calculations for keto/enol tautomerism were performed at the DFT/B3LYP level using 6-31++G(d,p) as a basis set. All the geometries including transition states (TS) were optimized without any constraints. The characteristics of the stationary points were analysed by vibrational frequency calculation. All the TSs showed one negative imaginary frequency vibrating in the directions of the reaction coordinate. All the  $\Delta G$  values were calculated at 298 K.

## **Results and discussion**

The crystal structure of 1 (crystallized from EtOH) shows keto form of this molecule, named as 1k (k = keto) (Figure 1a) 97 84 98 and 1283 8 monoclinic space group  $P2_1/n$ . The solid-state structure shows that the -OH hydrogen atom (H2A) of resorcinol moiety (C6-O1) near to azo group (-N=N-) has got transferred to the nitrogen atom (N2) and thus formed an intramolecular six-member ring  $(R_1^{1}(6))$  closed by a weak intramolecular hydrogen bonding interaction between N(2)-H(2A) and O1. Because of proton transfer to the N2, the N-N distance [1.3181(15) Å] is notably longer than normal azo-bond distances (-N=N-, 1.24-1.28Å) resulting into the formation of the keto form. Due to the formation of a six-member ring by O1-C6-C1-N1-N2-H(2A), the bond distances related to this ring are quite perturbed than their normal reported values as listed in Table S2. The N-H hydrogen atom (H2A) is also hydrogen bonded with an oxygen atom (O3) of nitro group forming another six-member ring (  $R_1^1(6)$ ). The AIM analysis (vide infra) shows that, there exist BCPs and RCPs formed by these intramolecular hydrogen bonds. In the crystal packing, there exists intermolecular hydrogen bonding between the O1 and hydrogen atom {H2' (' =  $\frac{1}{2}$  -x,  $\frac{1}{2}$  +y,  $\frac{1}{2}$  -z } of OH group of another symmetry related azo-molecule and formed 1D chain (Figure 1b) along crystallographic b direction. The details of hydrogen bonding distances and angles are represented in Table 3.



Fig. 1 (a) ORTEP view (with 50% ellipsoid probability) and (b) interactions in the solid-state in 1k.

Crystal structure of **2** (grown from DMF) shows the enol form, named as **2e** (e = enol)(Figure 2a). It crystallizes in triclinic space group  $P\overline{1}$ . The asymmetric unit (Figure 2a) contains one azomolecule and one DMF molecule. In the solid-state, there exist intra- and intermolecular hydrogen bonding interactions. The OH hydrogen atom (H1) of resorcinol moiety near to azo group (-N=N-) is hydrogen bonded with N1 atom and formed a six-membered ring enclosed by this interaction ( $R_1^1(6)$ ). The O1-H1<sup>...</sup>N1 distance is 1.81(2) Å. Here N(1)=N(2), N2-C8, C8-C9, and C9-O1 bond distances are as normal as reported in the literature (Table S2). The O3 of DMF molecule is hydrogen bonded with H2 of para-substituted OH

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group of azo-molecule. The AIM analysis (vide infra) of the asymmetric unit exhibits BCPs and RCPs of this interactions. In addition, there exist C-H···O/N interactions and  $\pi$ - $\pi$  stacking {Figure 2c; C7···C7' (-x, 1 - y, 1 - z) = 3.3868(17) Å and C8···C2' (1 - x, 1 - y, 1 - z) = 3.3623(17) Å}; and due to these interactions, it developed 1D chain (Figure 2b) along crystallographic c and a direction, respectively. The interactions have been reported in the Table 3.



(c) **Fig. 2** (a) ORTEP view(with 50% ellipsoid probability), (b) interactions in solid-state, and (c)  $\pi$ - $\pi$  stacking in **2e**.



We have also crystallized **2** from THF-acetonitrile (ACN) mixture named as **2-int** (int = intermediate) (Figure 3). It crystallizes in monoclinic space group  $P2_1/c$ . The asymmetric unit contains one azo-molecule only. Here the *ortho*-hydroxy group is hydrogen (H1) bonded with azo nitrogen (N2). But interestingly the O-H distance is 1.14(3) Å and the hydrogen (H1) is closer to azo nitrogen (N1) where the hydrogen bonding distance is 1.52(3) Å forming an intramolecular hydrogen bonded ring ( $R_1^1(6)$ ). AIM calculation (vide

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infra) shows that the  $\rho_c$  at BCP for this N1---H(1)-O interaction has been found to be **0.081** e Å<sup>-3</sup> which is more than of the state of the sta

The structural characterization of 3 (crystallized from DMA) shows enol form of it named as 3e (Figure 4a). It crystallizes in triclinic system with space group  $P\overline{1}$ . The asymmetric unit of it contains one molecule of azo-molecule and one DMA molecule and are connected through hydrogen bonds in the lattice. In the solid-state, there exist intra- and intermolecular hydrogen bonding interactions. The OH hydrogen atom (H1) of resorcinol moiety near to azo group (-N=N-) is hydrogen bonded with N2 atom and formed a six-membered ring enclosed by this interaction  $(R_1^1(6))$ . The O1-H1...N2 distance is 1.74(3) Å. The AIM analysis (vide infra) of the asymmetric unit exhibits BCPs and RCPs of this interaction. Here N(1)=N(2), N1-C6, C6-C1, and C1-O1 bond distances are as normal as reported in the literature (Table S2). In addition, there exist intermolecular hydrogen bonding interactions involving C-H···O/Cl interactions and as a result, it developed a hydrogen bonded 2D network in the solid-state (Figure 4b and 4c). The hydrogen bonding distances are represented in Table 3. There also exists C-H… $\pi$ interaction {C1…H13A' (' = 1-x,1-y,1-z) = 2.80 Å and C9…C15A'' ('' = x,y,-1+z = 2.88 Å}.





#### ARTICLE

**Fig. 4** (a) ORTEP view(with 50% ellipsoid probability), (b) interactions in the solid-state, and (c) C-H·· $\pi$  stacking in **3e**.

The structural characterization of 3 and 4 from THF-MeOH mixture shows keto form of those, named as 3k and 4k, respectively (Figure 5a and 5b). Both the compounds crystallize in monoclinic space group  $P2_1/n$  and they are isomorphous. As the structure **4k** was solved and refined using a data collected at 100.0(2) K, the structural features of 4k will be discussed here. The asymmetric unit of both contains one azo-molecule and one water molecule and they are hydrogen bonded to each other. The solid-state structure exhibits that the OH hydrogen atom (H1A) of resorcinol moiety near to azo group (-N=N-) has got transferred to the nitrogen atom (N1) and has formed a six-membered ring  $(R_1^1(6))$ ).enclosed by weak hydrogen bond interaction between N1-H(1A) and O2 where the distance is 1.90(4) Å. Because of hydrogen atom transfer to N1, the N-N distance [1.301(3) Å] is longer than normal azo-bond distances (Table S2). Due to six-member ring formation, the bond distances related to this interaction are perturbed than their normal literature reported values (Table S2). The O2 is hydrogen bonded with H3B of water molecule where the distance is 1.93(4) Å. The AIM analysis (vide infra) has been done using the asymmetric unit and it shows that there exist BCPs and RCPs formed by the intra-molecular interactions. In the crystal packing, there exist intermolecular hydrogen bonding between the O3 of water and hydrogen atom  $\{H1' (' = 1-x, 1-y, 1-z)\}$  (Table 3) of para-OH group of another symmetry related azo-molecule and formed 1D chain (Figure 5c and 5d) along crystallographic *a* direction.





Fig. 5 ORTEP view(with 50% ellipsoid probability) of (a) 4k, (b) 3k, and interactions in the solid-state of (c) 4k, (d) 3k.

#### 2. AIM calculations

The intra- and intermolecular interactions with lattice solvent molecules have been calculated using the AIM approach after optimizing the molecular conformation from the observed crystal structure. The calculations confirm the existence of BCP between the H atom and acceptor atom (N or O) and RCP has been also found in case of intramolecular interactions (Table 4). AIM analyses indicate that these interactions are of hydrogen bond type.

<b>Fable 4</b> AIM anal	ysis for the	compounds
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	Interactions	<b>ρ</b> c (at BCP) (e Å <sup>-3</sup> )	∇² <b>(ρ<sub>c</sub>)</b> (at BCP) (e Å⁻⁵)	<b>ρ</b> c (at RCP) (e Å <sup>-3</sup> )	∇² <b>(ρ<sub>c</sub>)</b> (at RCP) (e Å⁻⁵)
11	N2-H01	0.047	0.010	0.018	0.007
IK	N2-H <sup></sup> O3	0.022	0.005	0.014	0.005
2e	N1H-O1	0.046	0.008	0.018	0.007
2- int	N2 <sup></sup> H-O1	0.042	0.007	0.017	0.006
3e	N2H-O1	0.051	0.009	0.019	0.007
3k	N1-H <sup></sup> O2	0.059	0.012	0.020	0.008
4k	N1-H-02	0.058	0.012	0.020	0.008

#### 3. Proton transfer study

The UV-Vis spectra (ESI, Fig. S1) of the azo-compounds were recorded in dimethylacetamide (DMA) solvent using Lab India UV 3200 double beam UV-Vis spectrophotometer. The UV-Vis spectra exhibit mainly two peaks, one at ~400 nm characteristic for  $\pi \rightarrow \pi^*$ transition and another is at ~500 nm characteristic for  $n \rightarrow \pi^*$ transition. The crystal structure of 3k contains one water molecule, which is hydrogen bonded to O2 and the hydrogen atom (H1A) has been transferred to the N1 of the azo-group. So, this structure motivated us to study proton transfer in the ground state and directed us to think that the water molecule has a significant role in this transformation. Thus, we have recorded the UV-Vis spectra (ESI, Fig. S2) of all the compounds in DMA in the presence of water. The analysis of the spectra reveals that on increasing percentage of water, the peak for enol tautomer decreased and that for keto has increased. This could be possible if phenolic hydrogen (ortho- to the azo group) has been transferred to the nitrogen atom of the azo group. As the hydrogen atom is coordinated to the lone pair of the nitrogen atom, it may result in the decrease of  $n \rightarrow \pi^*$  transition peak. To get further confirmation, we have done TD-DFT calculations and it shows that the oscillator strengths (f) have been

decreased in the keto form for  $n \rightarrow \pi^*$  transition (Table 5). But in the case of **2**, there are no changes in  $n \rightarrow \pi^*$  transition. Then we have looked into the transition were  $\pi$ -orbital of azo-group is involved. There it exhibits a decrease of oscillator strengths (*f*) in the water medium (Table 6).

**Table 5** Calculated Oscillator Strengths (f) of the compounds in DMA and Water.

	The Peak for nπ*	Oscillator Strengths
	transition (nm)	(f)
<b>1</b> in DMA (1DMA)	429.33	0.2047
1 in Water (1W)	441.38	0.0017
<b>2</b> in DMA (2DMA)	430.9	0.0002
2 in Water (2W)	432.8	0.0002
<b>3</b> in DMA (3DMA)	398.44	0.5756
3 in Water (3W)	420.86	0.0054
4 in DMA (4DMA)	427.68	0.1183
<b>4</b> in Water (4W)	421.05	0.0016

Table 6 Calculated Oscillator Strengths (f) of 2 in DMA and Water.

			Peak involved for this Oscillator	
			transitions (nm) Strengths (f)	
2	in	DMA	407.92 0.6582	
(2DMA)				
2 in Water (2W)		<sup>-</sup> (2W)	447.40 0.2495	

**3k** and **4k** contain one water molecule in the asymmetric unit where **1k** does not have any lattice solvent molecule but still, transfer of hydrogen atoms was observed. Thus, to get insight about the role of substitutions and water molecule, DFT calculation has been performed. All the values obtained by theoretical calculation have been represented in the ESI Table S1a, 1b, 1c, and 1d for compound **1**, **2**, **3**, and **4**, respectively.

For this study, we have first considered the compound 3 as we were able to structurally characterize both enol (3e) and keto (3k) form, and 3k contains one lattice water molecule (O3) which is hydrogen bonded with keto carbonyl (O2). We have optimized the enol, keto, and transition state (TS) for all compounds without any constraints. First, we have calculated the thermodynamic parameters ( $\Delta G$ ,  $\Delta H$ and  $\Delta E$ ) for **3** without including the water molecule in the system. It reveals that enthalpy of formation ( $\Delta H = 0.68$  kcal/mol) and formation energy in term of electronic energy ( $\Delta E = 0.68$  kcal/mol) of keto form are positive. But when we have considered the water molecule in the system then it reduced the  $\Delta H$  (-2.85 kcal/mol) and  $\Delta E$  (-2.26 kcal/mol) values to negative. Similar results were also obtained in the case of 4. Thus, we can infer that the water molecule favoured the proton transfer process and the formation of keto form in the presence of water in the medium. In the case of 2, we found positive values for  $\Delta H$  and  $\Delta E$  where water molecule has not been included. When we have included the water molecule in the system then it also shows negative values for  $\Delta H$  and  $\Delta E$  even for the formation of keto form. We have tried to get the structure of the keto form of 2 from THF-ACN mixture and structural characterization of it (2-int) shows that O-H distance is 1.14(3) Å, which is closer to a transition state.

In case of **1**, it shows negative values for  $\Delta G$  (-1.31 kcal/mol)<sub>e</sub>  $\Delta H_{irle}$ 1.35 kcal/mol) and  $\Delta E$  (-1.35 kcal/mol) for the total tot

### Conclusions

Ground state proton transfer mechanism has been studied have experimentally and computationally. We both structurally characterized the intermediate for proton transfer by single crystal X-ray diffraction and experimentally demonstrated the same by UV-Vis spectroscopy. Further confirmation has been arrived at by computations. The hydrogen bonding and substitutions close to the azo group has monitored the proton transfer in the ground state. The interaction of the water molecule with the phenolic oxygen has weakened the O-H bond and strengthened the H-N bond. The effect of the substitutions is also similar like water in this proton transfer mechanism. The large size substitution has a large effect for this transformation. In the case of  $-NO_2$ , the hydrogen atom has been transferred totally to the nitrogen atom of the azo group. But in the case of -CN, the O-H bond is quite elongated towards the azo- group.

#### **Conflicts of interest**

There are no conflicts to declare.

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#### References

- 1 W.Szymański, J. M.Beierle, H. A. V.Kistemaker, W. A.Velema and B. L. Feringa, *Chem. Rev.*,2013,**113** (8), 6114–6178.
- 2 G.Mayer and A. Heckel, Angew. Chemie Int. Ed., 2006, 45 (30), 4900–4921.
- 3 C.Brieke, F.Rohrbach, A.Gottschalk, G.Mayer and A. Heckel, Angew. Chemie Int. Ed., 2012, 51 (34), 8446–8476.
- 4 L.Antonov, V.Deneva, S.Simeonov, V.Kurteva, D. Nedeltcheva and J. Wirz, Angew. Chemie Int. Ed., 2009, 48 (42), 7875–7878.
- 5 J.-M.Savéant and C. Tard, J. Am. Chem. Soc., 2014, **136** (25), 8907–8910.
- 6 C.Costentin, M.Robert and J.-M. Savéant, *Chem. Rev.*, 2010, **110** (12), PR1-PR40.
- 7 C.Costentin, S.Drouet, M.Robert, J.-M. Saveant, Science (80), 2012, 338 (6103), 90–94.
- 8 A. D.Wilson, R. H.Newell, M. J.McNevin, J. T.Muckerman, M. R.DuBois and D. L.DuBois, J. Am. Chem. Soc., 2006, 128, 358-388.

accepted

- 9 T.Liu, D. L.DuBois and R. M. Bullock, *Nat. Chem.*, 2013, **5** (3), 228–233.
- 10 S.Raugei, S.Chen, M.-H.Ho, B.Ginovska-Pangovska, R. J.Rousseau, M.Dupuis, D. L.DuBois and R. M. Bullock, *Chem. -A Eur. J.*, 2012, **18** (21), 6493–6506.
- 11 S.Lee, J.Lee and Y. Pang, Curr. Appl. Phys., 2015, 15 (11), 1492– 1499.
- 12 J.Wang, Q.Chu, X.Liu, C.Wesdemiotis and Y. Pang, *J. Phys. Chem. B*, 2013, **117** (15), 4127–4133.
- 13 F.Yu, P.Li, G.Li, G.Zhao, T.Chu and K. Han, J. Am. Chem. Soc., 2011, 133 (29), 11030–11033.
- 14 J.-S.Chen, P.-W.Zhou, G.-Y.Li, T.-S.Chu and G.-Z. He, J. Phys. Chem. B, 2013, 117 (17), 5212–5221.
- 15 M. X.Zhang and G. J. Zhao, J. Alloys Compd., 2016, 664, 439-443.
- 16 G. J.Zhao, K. L. Han, Acc. Chem. Res., 2012, 45, 404-413.
- 17 G. Y.Li, G. J.Zhao, K. L.Han and G. Z. He, J. Comput. Chem., 2011, 32, 668-674.
- 18 C.Ma, Y. G.Yang, C. Z.Li and Y. F.Liu, J. Phys. Chem. A,2015,119, 12686-12692.
- 19 G.Gilli, F.Belluccci, V.Ferretti and V. Bertolasi, J. Am. Chem. Soc., 1989, 111, 1023-1028.
- 20 P.Gilli, V.Bertolasi, V.Ferretti and G. Gilli, J. Am. Chem. Soc., 1994, 116, 909-915.
- 21 S.Steinwand, T.Halbritter, D.Rastädter, J. M.Ortiz-Sánchez, I.Burghardt, A.HeckelandJ. Wachtveitl,*Chem. - A Eur. J.*,2015, **21** (44), 15720–15731.
- 22 A. S.Özen, P.Doruker and V. Aviyente, J. Phys. Chem. A, 2007,111,13506-13514.
- 23 M.Han, S. J.Cho, Y.Norikane, M.Shimizu, A.Kimura, , T.Tamagawa and T. Seki, *Chem. Commun.*, 2014, **50**, 15815-15818.
- 24 M. J.Frisch, G. W.Trucks, H. B.Schlegel, G. E.Scuseria, M. A.Robb, J. R.Cheeseman, G.Scalmani, V.Barone, B.Mennucci, G. A.Petersson, H.Nakatsuji, M.Caricato, X.Li, H. P.Hratchian, A. F.Izmaylov, J.Bloino, G.Zheng, J. L.Sonnenberg, M.Hada, M.Ehara, K.Toyota, R.Fukuda, J.Hasega wa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A.Jr.Montgomery, J. E.Peralta, F.Ogliaro, M.Bearpark, J. J.Hevd.E.Brothers. К. N.Kudin, V. N.Staroverov, R.Kobayashi, J.Normand, K.Raghavachari, A.Rend ell, J. C.Burant, S. S.Iyengar, J.Tomasi, M.Cossi, N.Rega, J. M.Millam,M.Klene, F.Knox. 1. B.Cross, V.Bakken, C.Adamo, J.Jaramillo, R.Gomperts, R. E.Stratmann, O.Yazyev, A. J.Austin, R.Cammi, C.Pomelli, 1 W.Ochterski, R. L.Martin, K.Morokuma, V. G.Zakrzewski, G. A.Voth, P.Salvador, J. J.Dannenberg,S.Dapprich, Α. D.Daniels, Ö.Farkas, J. B.Foresman, J. V.Ortiz, J. Cioslowski, And D. J. Fox, Gaussian 09, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.
- 25 R.Denninng, T. Keith and J. Millam, *GaussView*, version 5; Semichem, Inc.: Shswnee Mission KS, 2009.
- (a) R. F. W.Bader, Atoms in Molecules: A Quantum Theory; 26 Clarendon Press, Oxford, 1990. (b) F.Biegler-König, J. Schönbohmand D. Bayles, AIM 2000 - A Program to Analyze and Visualize Atoms in Molecules, J. Comp. Chem., 2001, 22, 545-559. (c) F.Biegler-KönigandJ.Schönbohm, An Update to the AIM2000 - Program for Atoms in Molecules, J. Comp. Chem. 2002. (d) F.Biegler-König, T. T.Nguyen-Dang,Y.Tal and R. F. W.Bader, Calculation of the Average Properties of Atoms in Molecules, Journal of Physics B,1981,14, 2739-2751. (e) S. D.Cohen and A. C.Hindmarsh, CVODE, a Stiff/Nonstiff ODE Solver in C, Computers in 1996, 10, 2. (f) F.Biegler-Physics no. KönigandJ.Schönbohm,Atome in Molekülen einProgrammpaket, BerichteausLehre und Forschung, Nr. 8, Fachhochschule Bielefeld - University of Applied Sciences. (g) F. Biegler-König, Eigenschaften von Atomen in Molekülen,

BerichteausLehre und Forschung, Nr. 9, Fachhochschule Bielefeld - University of Applied Science Si: 10.1039/C8CE01878B

27 E.Cances, B.Mennucci and J. Tomasi, J. Chem. Phys., 1997, 107, 3032-3041.

T.Chu and K. Han,*J. Am. C* D–11033. -Y.Li, T.-S.Chu and G.-Z. He,*J.* 212–5221. hao,*J. Alloys Compd*.,2016,**664**,

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