



## Consideration on the optimized molecular geometry of photochromic Salicylaldehyde-p-hydroxybenzoyl hydrazone molecule by semi-empirical molecular orbital method MOPAC/MINDO3

Souad A. A. Bin-Sasi<sup>1\*</sup>, Mohamed S. Attia and M.S.A. Abdel-Mottaleb

*Nanophotochemistry and Solarchemistry Labs, Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt*

<sup>1</sup>(Permanent address: Faculty of Sciences Elmergib University, Zletin, Libya)

### ARTICLE INFO

#### Article history:

Received 25 September 2011

Accepted 16 November 2011

#### Keywords:

Keto-enol;

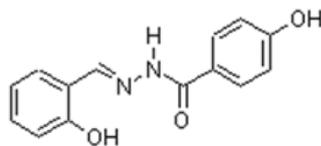
Hydrogen transfer;

Photochromism;

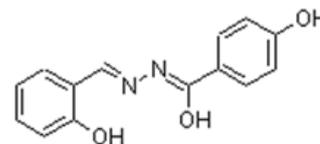
MOPAC MINDO/3 calculations.

### ABSTRACT

A MOPAC MINDO/3 calculation is performed for both  $S_0$  and  $S_1$  states to obtain the optimum molecular geometry of the keto-enol photochromic forms of Salicylaldehyde-p-hydroxybenzoyl hydrazone (1) and to explain the photo-induced hydrogen transfer to generate the corresponding enol form azine (2).



Form (1)



Form (2)

The azine (enol form) derived from the intramolecular hydrogen transfer of hydrazone (Heats of formations  $\Delta H = -430$  and  $-164$  kJ for  $S_0$  and  $S_1$  states, respectively) is found to be as stable as, or more stable than, the hydrazone form ( $\Delta H = -414$  and  $33$  kJ for  $S_0$  and  $S_1$  states, respectively). Furthermore, net charges, electron density distributions, ionization potentials and bond orders have been computed. The results explain well the H-transfer mechanism.

### Introduction

Different types of compounds including hydrazones exhibit photochromic behavior that may find different important applications<sup>1,2</sup>. Such compounds are known to exhibit keto-enol tautomerism under UV-Vis light irradiation. Recent experimental findings in our labs prompted us to carry out further theoretical studies attempting to explain the precise processes involved in the photochromic behavior of the compound under investigation.

The photochromic mechanism includes H-transfer<sup>3-6</sup>. Semi-empirical MO methods could be utilized to compute the optimum molecular geometry and to provide important theoretical information to explain stability and electronic distributions of the keto and enol forms leading to the photochromic behavior.

In this paper, the suitability of the H-transfer mechanism will be discussed using MOPAC MINDO/3 calculation.

\* Corresponding author.

E-mail address: [so3ad\\_Abdelsalam@hotmail.com](mailto:so3ad_Abdelsalam@hotmail.com)

### 2. Experimental

#### 2.1. Photochromism

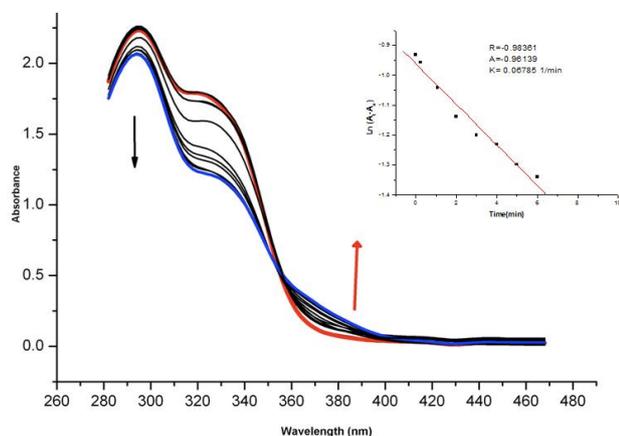
Full details of experimentation are described elsewhere<sup>7</sup>. We followed the absorption spectrum of the molecule using UBS 4000 Fiber Optics spectrophotometer, Ocean Optics, USA. The photochemical irradiation was derived from 120 W UVA and Visible lamps that stimulate the emission spectrum of Xenon lamps, which are fitted inside homemade Phocat 120 photoreactor.

#### 2.2. Computations

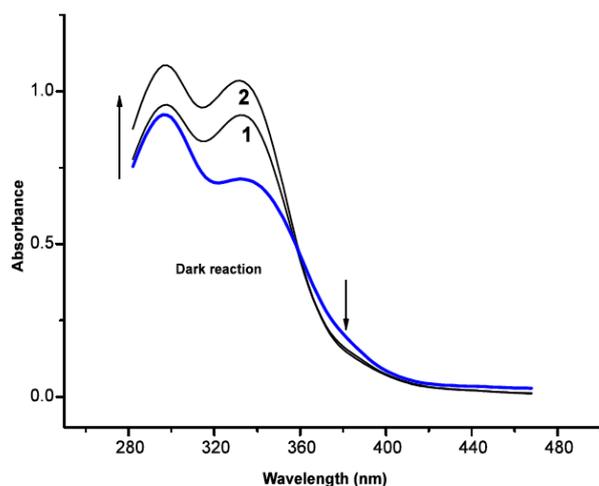
A semi-empirical MOPAC calculation<sup>8</sup> was applied to the hydrazone (1) and its enol form azine (2). The optimization of the structures was carried out using MOPAC MINDO/3 considering the valence shell electrons after the stabilization by Molecular Mechanics (force field parameter; MM2). Optimization of the geometries, in general, was performed for each of corresponding compounds to obtain the heat of formation.

### 3. Results and discussion

Figure (1) and Figure (2) show the photo induced fast forward reaction (rate =  $6.7 \times 10^{-2} \text{ min}^{-1}$ ) and the very slow dark back reaction (rate =  $\text{days}^{-1}$ ), respectively. The clear isosbestic points reveal the existence of keto-enol equilibrium responsible of the photochromic behavior of compound (1).

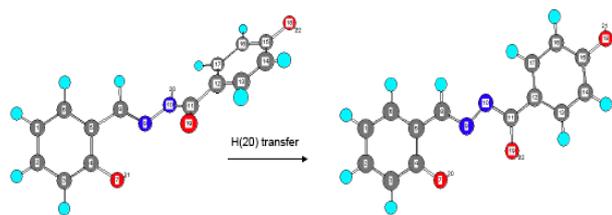


**Fig. 1:** Effect of light irradiation time on the absorption spectrum of  $5 \times 10^{-5}$  M solution of compound (1) in neutral aqueous medium of pH = 7. The inset shows the kinetics involved, which reveals first order rate at analytical wavelength = 380 nm.



**Fig. 2:** Dark back reaction followed by the absorption spectrum of  $5 \times 10^{-5}$  M solution of compound (1) in neutral aqueous medium of pH = 7 at one day intervals.

Figure 3 shows the structures of the two isomers under investigation (the keto form, namely; Salicylaldehyde-p-hydroxybenzoyl hydrazone (1) and the corresponding enol form azine (2)).



**Fig. 3:** Structure of the keto and enol forms of compound (1).

The optimized values of bond lengths, bond angles, and essential dihedral angles are given in Table 1. Heat of formations  $\Delta H$  and other computed parameters are given in Table 2. Table 3 and Table 4 contain Mulliken and net charges whereas Table 5 lists the bond orders. Referring to Figure 3, the step of hydrogen transfer from N(10) to the carbonyl oxygen(19) results in stabilizing the enol form (2) by -16 kJ in the  $S_0$  state whereas the  $S_1$  state that is generated under light irradiation exhibits much more pronounced stabilization by -193 kJ, see Table 2. Thus, the generally accepted action mechanism of a H-transfer is reasonable, in which the carbonyl oxygen traps the nearest H of interatomic distance value of 3.154 Angstrom to form thermodynamically more stable enol form azine (2) molecule than the starting hydrazone form (1). Further supportive parameter is the bond order value of N(10) – H(20), which is the weakest bond order amongst the other phenolic OH groups, see Table 5. Furthermore, Mulliken's charge populations of atomic orbitals<sup>9, 10</sup> are widely used tools for the interpretation of the internal structure of molecular orbital's. The computed values are listed in Table 3. It could be seen that the less positive the Mulliken charge of the H of a group is, the higher the transfer probability to the oxygen atom of the carbonyl is, the lower the stability of the hydrazone isomer is. It is novel and simple to evaluate the H-transfer sensitivity with the Mulliken charges of the H atoms of different groups; namely the NH and the phenolic groups. Moreover, computed net charges from the eigenvectors (see Table 4) are in agreement with the above correlation.

### 4. Conclusion

In the action mechanism of hydrazone molecule 1, which contains phenolic groups and NH group, MOPAC calculation under MINDO/3 potential function has well explained the H-transfer as follows:

1. H-transfer of NH group is the more favorable mechanism due to the thermodynamic stability gained. Enthalpy of formation reflects induced remarkable conjugation due to H-transfer.
2. Upon excitation of the hydrazone (1) by light absorption, the generated  $S_1$  state is thermodynamically unstable and tends to spontaneously stabilize by H-transfer to form the azine (2).
3. H-transfer from the phenolic groups is less favorable due to its large interatomic distances with carbonyl oxygen of the hydrazone molecule (1).
4. It is novel and simple to evaluate the H-transfer sensitivity with the Mulliken charges of the H atoms of different groups; namely the NH and the phenolic groups.

Table (1) Optimized bond lengths, bond angles, twist (dihedral) angles and Z-matrix

ATOM NUMBER (I)	CHEMICAL SYMBOL	BOND LENGTH (ANGSTROMS)		BOND ANGLE (DEGREES)		TWIST ANGLE (DEGREES)			
		NA:I		NB:NA:I		NC:NB:NA:I	NA	NB	NC
1	C								
2	C	1.40829	*				1		
3	C	1.39937	*	120.65195	*		2	1	
4	C	1.42535	*	119.31433	*	.00000	*	3	2
5	C	1.43607	*	121.98433	*	.00000	*	4	3
6	C	1.40035	*	119.33006	*	-.31648	*	1	2
7	O	1.32408	*	112.91646	*	-179.55287	*	4	3
8	C	1.48784	*	123.77832	*	-178.62091	*	5	4
9	N	1.26672	*	119.57136	*	-94.64084	*	8	5
10	N	1.29010	*	130.33180	*	-178.21001	*	9	8
11	C	1.36850	*	124.07382	*	-178.65762	*	10	9
12	C	1.50470	*	115.18780	*	-179.36754	*	11	10
13	C	1.42664	*	122.20465	*	92.58458	*	12	11
14	C	1.40016	*	123.52304	*	176.84965	*	13	12
15	C	1.42314	*	119.15172	*	.00000	*	14	13
16	C	1.41872	*	119.35805	*	.00000	*	15	14
17	C	1.42249	*	122.44420	*	-91.04936	*	12	11
18	O	1.32237	*	115.50603	*	179.99963	*	15	14
19	O	1.21689	*	121.91789	*	.44762	*	11	10
20	H	1.05014	*	121.26744	*	1.22572	*	10	9
21	H	.94983	*	116.09529	*	177.54732	*	7	4
22	H	.95134	*	114.29954	*	178.99860	*	18	15
23	H	1.10458	*	121.45802	*	-179.99963	*	16	15
24	H	1.10364	*	119.05205	*	-179.99963	*	14	13
25	H	1.10835	*	119.63780	*	3.19630	*	17	12
26	H	1.10828	*	119.36328	*	-3.18233	*	13	12
27	H	1.10402	*	119.35104	*	-179.68402	*	3	2
28	H	1.10620	*	119.98752	*	179.99963	*	2	1
29	H	1.10352	*	120.44388	*	179.68402	*	1	2
30	H	1.13023	*	113.20148	*	87.01027	*	8	5
31	H	1.10803	*	118.11833	*	179.68402	*	6	1

Table (2) Some important calculated MO parameters\*

Molecular form	Heat of formation (kJ)	Ionization potential (eV)	HOMO (eV)	LUMO (eV)
Hydrazone-S <sub>0</sub>	-414.9077	8.49	-8.47845	0.658
Hydrazone-S <sub>1</sub>	33.799	1.89	-1.89080	0.788
Hydrazine-S <sub>0</sub>	-430.8404	7.61	-7.60755	0.843
Hydrazine-S <sub>1</sub>	-160.6576	1.53	-1.5336	0.836

\*HOMO and LUMO orbitals of hydrazone form in the S<sub>0</sub> state are mainly composed of orbital contributions localized on the phenolic ring C1-C6 and N(9), whereas HOMO and LUMO of the hydrazine form are mainly composed of contributions of all orbitals distributed over the whole molecule.

Table (3) MULLIKEN NET ATOMIC CHARGES

ATOM NO.	NET CHARGE			
	HYDRAZONE (1)		HYDRAZINE (2)	
	S <sub>0</sub>	S <sub>1</sub>	S <sub>0</sub>	S <sub>1</sub>
C(1)	-.069798	.129995	-.071540	-.069516
C(2)	.082607	-.109519	.077851	.073129
C(3)	-.130007	.402235	-.131824	-.129930
C(4)	.412813	.402235	.406912	.388064
C(5)	-.140564	-.126086	-.137790	-.088770
C(6)	.085204	-.027015	.078434	.063613
O(7)	-.495074	-.449666	-.498998	-.498673
C(8)	.127765	.116293	.110050	-.126871
N(9)	-.033992	-.029018	-.026679	.101446
N(10)	-.161403	-.166889	-.202789	-.198048
C(11)	.691484	.689989	.483587	.480239
C(12)	-.199789	-.199051	-.148957	-.164036
C(13)	.122409	.121951	.100678	.107911
C(14)	-.143415	-.143438	-.141140	-.142216
C(15)	.432357	.431204	.426952	.426456
C(16)	-.190004	-.189951	-.187224	-.185918
C(17)	.136240	.135318	.117186	.114238
O(18)	-.490546	-.490875	-.490979	-.491490
O(19)	.013176	-.591180	-.545493	-.540611
H(20)	.013176	.012358	.278387	.274985
H(21)	.274903	.281534	.277226	.277519
H(22)	.277767	.277382	.259616	.264680
H(23)	.026386	.025402	.024837	.021530
H(24)	.044825	.044184	.042702	.043498
H(25)	-.020149	-.021512	-.016840	-.019061
H(26)	-.015328	-.015328	-.015558	-.019235
H(27)	.040542	.028607	.036108	.030392
H(28)	-.012046	.010764	-.016416	-.018853
H(29)	.010282	-.017052	.004700	.000896
H(30)	-.072258	-.066831	-.073788	.046913
H(31)	-.014826	-.002126	-.019209	-.022281

Table (4) NET ATOMIC CHARGES

C(1)	-.071613	.142488	-.073496	-.071725
C(2)	.075374	-.133195	.070005	.065783
C(3)	-.125140	-.064787	-.127100	-.126111
C(4)	.392668	.405914	.387304	.371107
C(5)	-.128482	-.131164	-.123714	-.084976
C(6)	.072102	-.043900	.65893	.053313
O(7)	-.445832	-.396492	-.449762	-.449373
C(8)	.091979	.083254	.072073	-.164333
N(9)	.005020	.009264	.012059	.151204
N(10)	-.100608	-.106669	-.164358	-.156660
C(11)	.627163	.625294	.422827	.416012
C(12)	-.172194	-.172322	-.128226	-.145264
C(13)	.104362	.103810	.086869	.094080
C(14)	-.138369	-.138131	-.136676	-.137288
C(15)	.416263	.415647	.411339	.411184
C(16)	-.177606	-.177517	-.175181	-.174296
C(17)	.114226	.094708	.099109	.094708
O(18)	-.440904	-.441813	-.441440	-.441813
O(19)	-.564314	-.565624	-.498041	-.492591
H(20)	-.006842	-.007519	.251124	.247903
H(21)	.247872	.253915	.250655	.250890
H(22)	.251177	.250769	.233476	.238356
H(23)	.021347	.020579	.020020	.017003
H(24)	.036510	.036006	.034688	.035553
H(25)	-.017958	-.019056	-.015481	-.016998
H(26)	-.014151	-.014136	-.014518	-.017523
H(27)	.033005	.023743	.029377	.024460
H(28)	-.009159	.010348	-.012718	-.014682
H(29)	.009946	-.012633	.005348	.002255
H(30)	-.072097	-.066706	-.073968	.039822
H(31)	-.013748	-.003210	-.017487	.019999

Table (5) Bond Orders of different isomeric forms of compound (1) in the ground and first singlet excited states

Atom	Bond	Hydrazone-		Hydrazine	
		S <sub>0</sub>	S <sub>1</sub>	S <sub>0</sub>	S <sub>1</sub>
C <sub>1</sub>	C <sub>1</sub> —C <sub>2</sub>	1.357268	1.083401	1.367020	1.379896
	C <sub>1</sub> —C <sub>6</sub>	1.424995	1.507412	1.413205	1.428427
	C <sub>1</sub> —H <sub>29</sub>	.939125	.946698	.939019	.948390
C <sub>2</sub>	C <sub>2</sub> —C <sub>3</sub>	1.430096	1.380625	1.421688	1.435018
	C <sub>2</sub> —H <sub>28</sub>	.936588	.947881	.936307	.946007
C <sub>3</sub>	C <sub>3</sub> —C <sub>4</sub>	1.298046	1.306986	1.305820	1.318835
	C <sub>3</sub> —H <sub>27</sub>	.939818	.948876	.939880	.948309
C <sub>4</sub>	C <sub>4</sub> —C <sub>5</sub>	1.309679	.951948	1.304351	1.297904
	C <sub>4</sub> —O <sub>7</sub>	.984692	1.054619	.982849	.992053
C <sub>5</sub>	C <sub>5</sub> —C <sub>6</sub>	1.340369	1.211932	1.354045	1.357848
	C <sub>5</sub> —C <sub>8</sub>	.938818	.991254	.939407	.970602
C <sub>6</sub>	C <sub>6</sub> —H <sub>31</sub>	.937477	.948626	.937129	.946494
	O <sub>7</sub> —H <sub>20</sub>	—	—	.907280	.917534
C <sub>8</sub>	O <sub>7</sub> —H <sub>21</sub>	.908525	.913750	—	—
	C <sub>8</sub> —N <sub>9</sub>	1.881828	1.877367	1.831381	1.375082
N <sub>9</sub>	C <sub>8</sub> —H <sub>30</sub>	.869535	.848431	.864201	.840770
	N <sub>9</sub> —N <sub>10</sub>	1.037655	1.033849	1.143251	1.363719
N <sub>10</sub>	N <sub>10</sub> —C <sub>11</sub>	1.080526	1.088445	1.698313	1.365350
	N <sub>10</sub> —H <sub>20</sub>	.904091	.913322	—	—
C <sub>11</sub>	C <sub>11</sub> —C <sub>12</sub>	.895809	.902925	.912732	.898059
	C <sub>11</sub> —O <sub>19</sub>	1.607448	1.623303	.898175	.912621
C <sub>12</sub>	C <sub>12</sub> —C <sub>13</sub>	1.337402	1.351087	1.338841	1.340786
	C <sub>12</sub> —C <sub>17</sub>	1.364003	1.378128	1.363063	1.361139
C <sub>13</sub>	C <sub>13</sub> —C <sub>14</sub>	1.433310	1.448165	1.430767	1.443872
	C <sub>13</sub> —H <sub>26</sub>	.936717	.946557	.936816	.946314
C <sub>14</sub>	C <sub>14</sub> —C <sub>15</sub>	1.295375	1.309162	1.298123	1.310418
	C <sub>14</sub> —H <sub>24</sub>	.939823	.949689	.939811	.948521
C <sub>15</sub>	C <sub>15</sub> —C <sub>16</sub>	1.320620	1.334720	1.321221	1.334142
	C <sub>15</sub> —O <sub>18</sub>	.991214	1.001054	.989509	.999510
C <sub>16</sub>	C <sub>16</sub> —C <sub>17</sub>	1.406229	1.420595	1.406871	1.420940
	C <sub>16</sub> —H <sub>23</sub>	.939591	.949410	.939573	.947393
C <sub>17</sub>	C <sub>17</sub> —H <sub>25</sub>	.936364	.946104	.936754	.946170
	O <sub>18</sub> —H <sub>21</sub>	—	—	.909227	.918656
O <sub>19</sub>	O <sub>18</sub> —H <sub>22</sub>	.908886	.918624	—	—
	O <sub>19</sub> —H <sub>22</sub>	—	—	.900462	.892933

## References

- 1) K. Uz'arević, M. Rubc'ić, V. Stilinović, B. Kaitner, M. Cindric, 2010: Keto–enol tautomerism in asymmetric Schiff bases derived from p-phenylenediamine, *J. Mol. Struct.* 984, 232–239.
- 2) R.S. Stoll, S. Hecht, 2010: Artificial light-gated catalyst systems, *Angew. Chem. Int. Ed.* 49: 5054 – 5075.
- 3) S.C. Bhatia, J.M. Bindlish, A.R. Saini, P.C. Jain, 1981: *J. Chem. Soc. Dalton Trans.* 1773.
- 4) J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, 1992: *Coord. Chem. Rev.* 119: 67.
- 5) M. Yıldız, Z. Kılıç, T. Hökelek, 1998: *J. Mol. Struct.* 441: 1.
- 6) M. Gavranic', B. Kaitner, E. Meštrovic', 1996: *J. Chem. Crystallogr.* 26: 23.
- 7) Suoad Bin-Sasi, M.Sc. thesis, Department of Chemistry, Faculty of Science, Ain Shams University (2011 – under preparation).
- 8) J.J.P. Stewart, 1992: CICPE, No. 455, Version 6.0, Department of Chemistry, Indiana University, Bloomington, IN.
- 9) R.S. Mulliken, 1955: *J. Chem. Phys.* 23: 1833.
- 10) R.S. Mulliken, 1955: *J. Chem. Phys.* 23: 1841.