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Crystal structure and feasibility of intramolecular proton transfer reaction of salicylaldazine

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Abstract

The work describes characterization of salicylaldazine by IR, NMR and single crystal X-ray diffraction studies. The compound crystallizes in the monoclinic crystal system with the space group $P2_1/n$, $a = 8.554(3)$, $b = 6.338(2)$, $c = 11.864(5)$ Å, and $\beta = 107.89(2)°$. There are two strong intramolecular hydrogen bonds of the type O–H···N and two weak hydrogen bridges of the type C–H···O which help the molecules to pack in a layered structure. Semi-empirical calculations have been performed to predict theoretically the feasibility of intramolecular ground and/or excited state proton transfer reaction/s. Potential energy curves have been generated in the ground (S_0) and the lowest excited (S_1) singlet states to judge the feasibility of intramolecular single and double proton transfer reactions. Semi-empirical (AM1) calculations suggest that only the excited state intramolecular single proton transfer process is favored both thermodynamically and kinetically. No other prototropic processes are theoretically feasible.

Keywords: Salicylaldazine; Intramolecular proton transfer; Hydrogen bonding; Potential energy curve

1. Introduction

Self-assembly by H-bonding and van der Waals' interaction is a very important process for the formation of biological architecture [1–3]. Hydrogen bonds are so widespread in chemistry and biology and have so many structural and mechanistic consequences that they have been rapidly outpaced by observations concerning what they can do [4,5]. These mechanisms are being developed as efficient design tools in material science for organizing individual molecular motifs into highly ordered supramolecules.

Aldazines are the ligands obtained by condensation of aromatic aldehydes with hydrazines. These compounds are known to behave as tridentate chelating agents, in which either of the two azine nitrogens coordinates along with the two pyridine nitrogens [6]. The molecules are coplanar because of the high degree of conjugation and therefore coordinate along an edge.

Osborn and Youinou showed that the ligand 3,6-di-(2-pyridyl)pyradazine (dppn) forms 2×2 grid arrays with tetrahedral metal ions [7], a concept which Baxter et al. elegantly extended to create higher order $N \times N$ grid arrays [8]. In contrast to dppn with its rigid central ring, aldazines have the freedom to rotate about their N–N central bond and so permit formation of architectures other than the grid arrays. An interesting feature of the ligand, salicylaldazine, is that due to the presence of OH groups close to the azine nitrogens, which exhibit a trans orientation, there are ample possibilities for intramolecular hydrogen bonding. There is also the possibility that intramolecular proton transfer (IPT) might take place between these two groups. A cursory look at the symmetrical molecular structure would suggest the possibility of intramolecular single as well as double proton transfer (DPT) reactions. Hence, characterization of these ligands from spectroscopic and X-ray diffraction studies is important from structural point of view. The aim of this article is to study the structural aspects of salicylaldazine and also to find out theoretically the feasibility of the ground state and the excited state intramolecular prototropic processes.

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2. Experimental

Starting materials for the synthesis of salicylaldazine, namely, salicylaldehyde (Merck, India) and hydrazine hydrate 80% GR (Loba, India) were used as received. Solvents like methanol and tetrahydrofuran (Merck, India) were of reagent grade and dried by standard methods. Salicylaldazine was synthesized by condensation of hydrazine hydrate and salicylaldehyde in a 1:2 molar ratio in methanol. The yellow powder-like product was filtered-off and washed with methanol. The block-shaped single yellow crystals for X-ray analysis were obtained from slow evaporation of a tetrahydrofuran solution. FTIR (KBr) signals were consistent with the observations of Abo Ali [9]. ^{1}H NMR (in $CDCl_3$, 300 MHz): $\delta = 6.95-7.05$ (m, 2 H, arom.H), 7.26–7.42 (m, 2 H, arom.H), 8.70 (s, 1 H, aliph. H), 11.38 (s, 1 H, phenolic H). ^{13}C NMR (in $CDCl_3$, 75 MHz): $\delta = 117.05$ (C6, arom.), 117.17 (C2, arom.), 119.62 (C4, arom.), 132.45 (C3, arom.), 133.34 (C5, arom.), 159.69 (C7, arom.), 164.6 (C1, aliph.).

2.1. Crystal data collection and refinement

Intensity data for yellow salicylaldazine was collected for 1934 reflections (1383 unique reflections) at 293(2) K on a Siemens P4 diffractometer using graphite monochromatized Mo Kα radiation (0.71073 Å). The employed $\omega-2\theta$ scan mode was in the range $3.69 \leq \theta \leq 27.5°$. No decomposition of the crystal during the data collection was noted. The intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods with SHELXS-97 and non-hydrogen atoms refined anisotropically by full matrix least-squares on F^2 using SHELXS-97.[1] Refinements give $R_1 = 0.043[I > 2\sigma(I)]$ and $wR_2 = 0.124$ (all data) for salicylaldazine. Final refinement details are given in Table 1. The maximum and minimum peaks in the final difference map were 0.232 and -0.139 e Å^{-3}. Crystallographic data for the compound has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 224827). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code + 44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk).

2.2. Theoretical calculations

Although, ab initio calculations involving extended basis sets with extensive configuration interaction (CI) have been successful in explaining structures, energetics and reactivities of small molecules in different electronic states, such reports are still limited in number for large molecular systems. Semi-empirical molecular orbital methods have already established their wide usefulness in this respect. The methods provide acceptable approximations to give results quite close to the experimental findings [10–16]. The reliability of the method of calculation (AM1-SCI) has already been established through studies on different types of molecular systems varying in their photophysical properties. For the present calculations, we have used the commercial package, HyperChem 5.01 (Hypercube Inc., Canada). The geometry of the molecule has been optimized in the ground state using the AM1 method. AM1-SCI has been adopted for the calculation of the excited state energies. It is pertinent to mention here that present calculations have been performed for the free molecule in vacuum only and no specific interactions like hydrogen bonding etc. have been taken into account.

[1] O–H and C–H distances of 0.82 and 0.93 Å were employed by SHELX for the calculation of the respective H atom positions.

Table 1
Crystal data, structure solution and refinement parameters for $C_{14}H_{12}N_2O_2$

Empirical formula	$C_{14}H_{12}N_2O_2$
Formula weight	120.13
Color, habit	Yellow
Crystal size/mm	$0.66 \times 0.51 \times 0.61$
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.554(3)$ Å, $\alpha = 90°$; $b = 6.338(2)$ Å, $\beta = 107.89(2)°$; $c = 11.864(5)$ Å, $\gamma = 90°$
Volume (Å^3)	612.0(4)
Z	2
Density (calc., Mg m^{-3})	1.304
Absorption coefficient (mm^{-1})	0.089
$F(000)$	252
Diffractometer (Siemens P4)	
Temperature (K)	293(2)
θ range (°) for data collection	3.69–27.49
Limiting indices	$-11 \leq h \leq 1, -1 \leq k \leq 8, -15 \leq l \leq 15$
Reflections collected/unique	1934/1383, R(int) = 0.0339
Completeness to theta = 27.49	98.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1383/0/89
Goodness-of-fit on F^2	1.052
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0426$, $wR2 = 0.1156$
R indices (all data)	$R2 = 0.0564$, $wR2 = 0.1243$
Extinction coefficient	0.06(3)
Largest diff. peak and hole (e Å^{-3})	0.232 and -0.139

3. Results and discussion

3.1. Description of the structures

Salicylaldazine crystallizes in the monoclinic space group $P2_1/n$. Table 1 lists the crystallographic data and refinement parameters and Table 2 presents selected bond lengths and bond angles. The crystallographic parameters are consistent with the reports of Xu et al. [17]. The calculated values of the parameters for the optimized structure are given in italics. The calculated values are in

Table 2
Selected bond lengths (Å) and angles (°)

N1–C1	1.284(2)/*1.307*
N1–N1_a	1.404(2)/*1.345*
C1–C2	1.454(2)/*1.462*
C7–O7	1.350(2)/*1.367*
N1–C1–C2	121.40(1)/*123.0*
N1–C1–H1	119.3/*123.5*
C1–N1–N1_a	113.51(1)/*118.7*
C2–C1–H1	119.3/*113.6*
C3–C2–C1	120.05(11)/*116.3*
C7–C2–C1	121.59(11)/*125.6*

reasonable agreement with the X-ray structural data. The deviation between the two sets is assigned to the crystal field stabilization and intra and intermolecular hydrogen bonding effects. Fig. 1 shows the ORTEP view with atom numbering of the salicylaldazine, which was drawn using 25% probability ellipsoids.

The basic features of the molecular structure do not differ from those of the expected structure. The two benzene rings are coplanar and are in trans configuration with C1–N1 and C1_a–N1_a bonds relative to N1–N1_a, which may be due to stabilization via intramolecular O–H···N hydrogen bonds between N1 and H7–O7 and also N1_a and H7_a–O7_a···O7–H7 acts as a donor in the three-centre O7–H7···N1 interaction which is intramolecular in nature, and coplanar with the adjacent benzene ring (C1–N1–N1_a–C1_a: 179.98(12)°, N1_a–N1–C1–C2: 179.88(11)°, N1–C1–C2–C3: 179.54(12)°, N1–C1–C2–C7: 1.32(19)°). In a second hydrogen bond, O7 acts as an acceptor in a three-centre C1–H1···O7 interaction, which is intermolecular in nature, connecting the molecule to a symmetry-related one (symmetry code: $-1/2+x$, $1/2-y$, $-1/2+z$).

The structure determination reveals that the 2D crystal structure consists of individual chains. In each chain, two phenolic oxygen atoms of each molecule form very weak hydrogen bridges with aliphatic hydrogen atoms of two adjacent molecules, thus forming a polymeric chain (C1–H1···O7: 3.366(2) Å and 167°) along the *a*-axis (Fig. 2). Although, C1–H1···O7 distance seems to be large compared to the normal intermolecular hydrogen bonding systems, recent experiments have revealed that the C···O distance in C–H···O hydrogen bond can be as large as 4.0 Å [18]. There is no visible π–π interaction between such a chain and its two immediate neighbors, as the distance between neighboring benzene ring is ~6.5 Å.

AM1 optimization of the structure of salicylaldazine molecule assigns a C_{2h} symmetry to the molecule. This is supported by the crystal structure analysis. This leads to the possibility of the molecular system being vulnerable to a single and/or DPT reaction in the ground state and/or excited state. To examine theoretically, the possibilities of these processes, we have simulated the potential energy curves (PEC) for the prototropic processes in both ground state (S_0) and the lowest excited singlet state (S_1). For the intramolecular single proton transfer (SPT) reaction, the N1–H7 (R_{1-7}) distance has been considered as the reaction coordinate. For the intramolecular DPT both N1–H7 (R_{1-7}) and N1_a–H7_a distances have been treated as reaction coordinates. However, considering the symmetric structure of the molecule, variation of both the distances has been kept same in each stage. For the generation of the PEC for the IPT process, we have optimized the geometry with various preset values of the reaction coordinate. Fig. 3 depicts the simulated PECs for the intramolecular single and DPT processes of the isolated molecule in the S_0 and S_1 states. The figure clearly reveals that the tautomer formation through intramolecular SPT in the ground state leads to endothermicity ($\Delta H_{\text{calc.}} = 10.4$ kcal mol^{-1}). However, the reaction becomes exothermic in the S_1 state ($\Delta H_{\text{calc.}} = -9.2$ kcal mol^{-1}). Thus, the SPT reaction is thermodynamically unfavorable in the ground state but it is

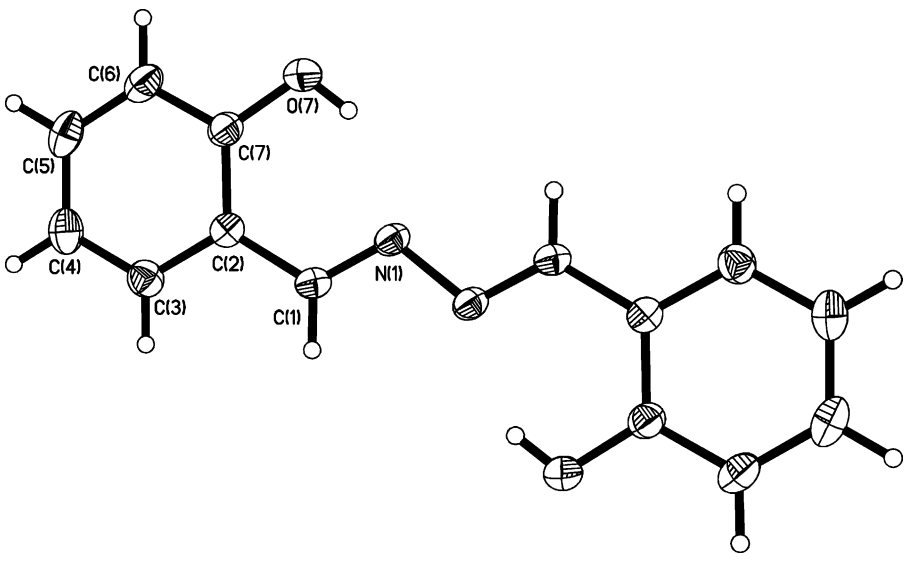

Fig. 1. ORTEP view with atom numbering of the salicylaldazine, drawn using 25% probability ellipsoids.

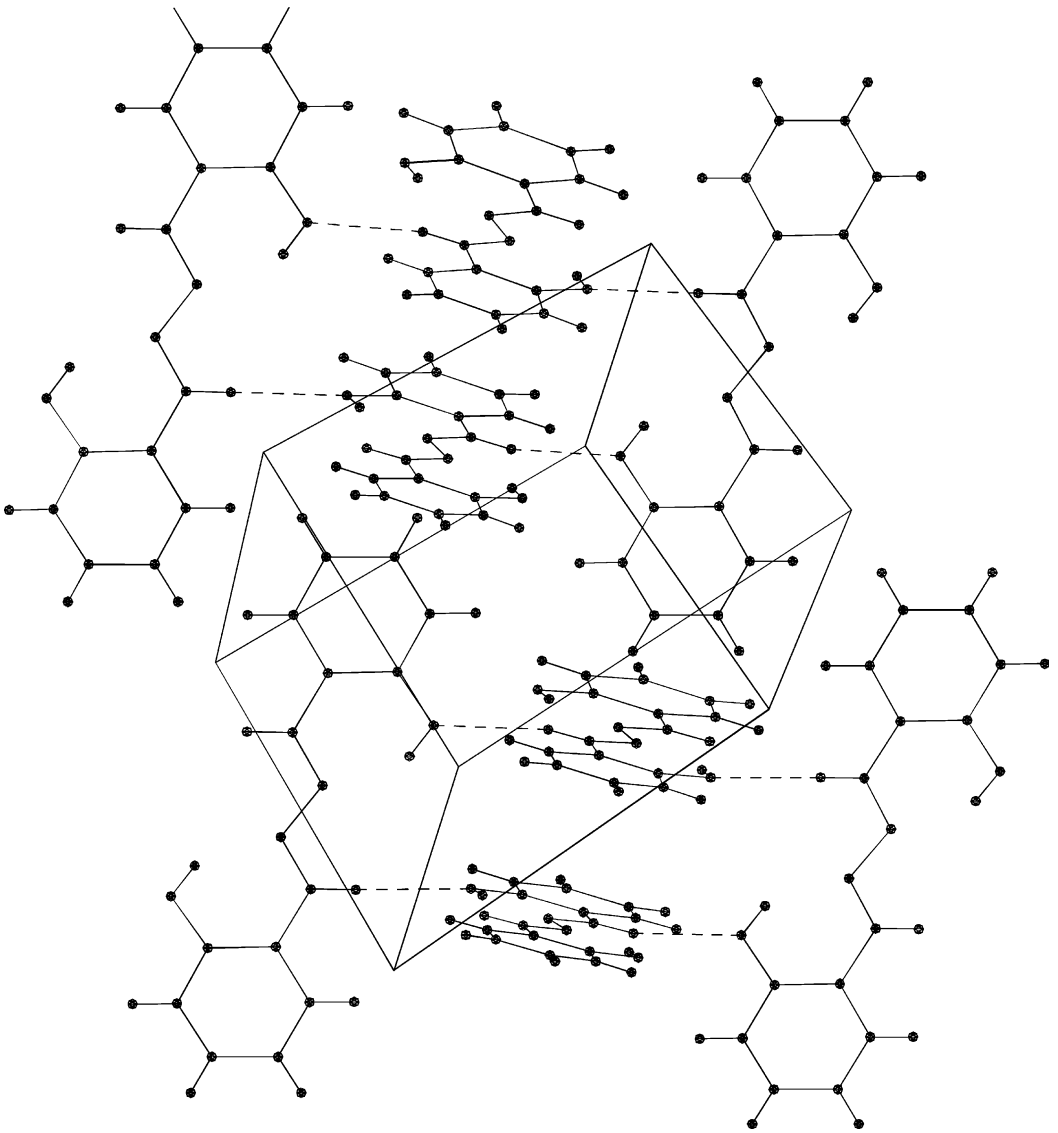

Fig. 2. Formation of chains through weak intermolecular C–H···O hydrogen bridges.

favored in the S_1 state. Considering the kinetic aspect of the same reaction the calculation reveals that the activation energy for the process is quite high (21.9 kcal mol^{-1}) which is unattainable under the normal situations. This high activation barrier imposes a kinetic restriction on the occurrence of the process in the ground state. This barrier is, however, reduced appreciably in the lowest excited singlet state. The calculated activation barrier is 11.2 kcal mol^{-1} which is nearly half the barrier experienced in the ground state. Thus, both the thermodynamic as well as the kinetic factors suggest that the intramolecular SPT is feasible in the S_1 state although it is improbable in the ground state.

A similar treatment for the intramolecular DPT reaction, as represented in the same figure, indicates that the DPT process is endothermic in both the S_0 and S_1 states amounting to $\Delta H_{calc.} = 29.6$ and 13.6 kcal mol^{-1}, respectively. Although, the endothermicity is reduced remarkably in the excited state, thermodynamics do not favor the IDPT process

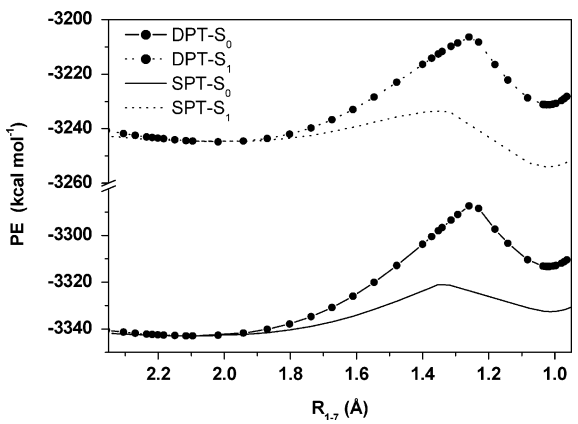

Fig. 3. Potential energy curves for the proton transfer process of salicylaldazine in S_0 and S_1 states. SPT and DPT represent single and double proton transfer, respectively.

in either of the two states. The activation energies for the IDPT process are calculated to be 55.6 and 38.4 kcal mol^{-1} in S_0 and S_1 states, respectively. Both of the barriers corresponding to the two electronic states are too high to allow a kinetic process to take place. It is thus apparent that the DPT process is not feasible in either of the S_0 and S_1 states because of both thermodynamic and kinetic factors.

The simulated PEC, thus, suggest that salicylaldazine is susceptible to excited state intramolecular SPT but in spite of being symmetric the corresponding DPT is unfavorable both from thermodynamic as well as kinetic points of view.

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