Synthesis, crystal structure and feasibility of intramolecular proton transfer reaction of salicylaldazine

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Abstract

The work describes the synthesis and characterization of salicylaldazine by CHN analysis, IR, NMR and single crystal X-ray diffraction. The compound $C_{14}H_{12}N_2O_2$ crystallizes in the monoclinic crystal system with the space group $P2_1/n$, a = 8.554(3) Å, b = 6.338(2) Å, c = 11.864(5) Å, and β =107.89(2)^0. There are two strong intramolecular hydrogen bonds of the type O−H···N and two intermolecular hydrogen bonds of the type C−H···N which help the molecules to pack in a layered structure. Semi-empirical calculations have also 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) 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.

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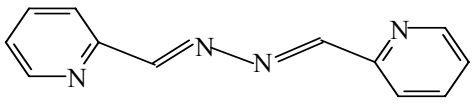
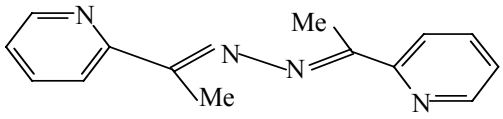
Introduction

Self-assembly by H-bonding and Van der Waal's interactions are very important processes for the formation of biological architecture.[1] 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.[2,3] These mechanisms are being developed as efficient design tools in material science for organizing individual molecular motifs into highly ordered supramolecules.

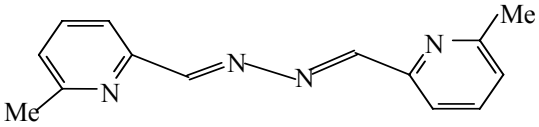
Aldazines (**1-3, 5**) are the ligands obtained by condensation of an aromatic aldehyde with hydrazine. In the case of **1** – **3**, these compounds might be expected to behave as a tridentate chelating agent, in which either of the two azine nitrogens might coordinate, along with the two pyridine nitrogens.[4] The molecules could also be expected to be coplanar because of the high degree of conjugation and therefore should coordinate along an edge.



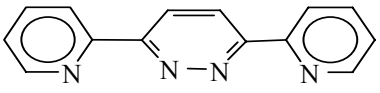
2- pyridinealdazine(1)



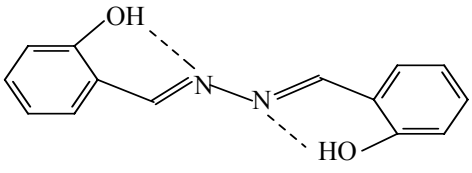
pyridylmethylketazine (2)



6-methyl-pyridinealdazine(3)



3, 6-di(2-pyridl)pyradazine(4)



Salicylaldazine(5)

Osborn and Youninou showed that the dppn ligand (4) forms 2 x 2 grid arrays with tetrahedral metal ions,[5] a concept which Lehn elegantly extended to create higher order N x N grid arrays.[6] 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. All these ligands have not been structurally characterized by X-ray diffraction so far. An interesting feature of ligand (5) 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 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 reactions. The aim of this article is to study the structural aspects of this interesting ligand and also to find out theoretically the feasibility of the ground state and the excited state intramolecular prototropic processes.

Experimental

Materials and methods

Starting materials for the synthesis of compound (1), *viz*., 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 before use.

Physical measurements

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. Infrared spectrum (400-4000 cm^{-1}) was recorded from KBr pellets on a Nickolet Magna

IR 750 series-II FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT 300 MHz NMR spectrometer.

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[7-13]. 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.

Synthesis of Compound

Salicylaldazine was synthesized by stirring a methanol (15 ml) solution of salicylaldehyde (0.244g, 2.0 mmol) with hydrazine (0.05g, 1mmol, 80%). The yellow powder-like product was filtered off and washed with methanol. The block-shaped single

yellow crystals for X-ray analysis were obtained by the slow evaporation of a tetrahydrofuran solution. Anal. calcd. For $C_{14}H_{12}N_2O_2$: C, 70.0; H, 5.0; N, 11.7; found C, 69.45; H, 5.12; N, 11.55%. FTIR (KBr) ν/cm^{-1}: 1278.7 (C -O_{phe}), 1487 (C=C_{aro}), (1624 vs 1571.9 (C=N), 2972 (C-H_{alip}), 3043.5 vs 752 (C-H_{aro}) and 2844–3043 (O−H···N hydrogen bonding). 1H NMR: δ = 6.95-7.05 (m, 2 H, armo.H), 7.26-7.42 (m, 2 H, armo.H), 8.70 (s, 1 H, aliph. H), 11.38 (s, 1 H, phenolic H). ^{13}C NMR: δ = 117.05 (C25, armo.), 117.17 (C21, armo.), 119.62 (C23, armo.), 132.45 (C22, armo.), 133.34 (C24, armo.), 159.69 (C26, armo.), 164.6 (C1, alip.).

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 difractometer using graphite monochromatized MoKα radiation (0.71073 A^0). The employed ω-2θ scan mode was in the range $3.69 \leq \theta \leq 27.49^0$. 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 SHELXL-97. Hydrogen atoms were included in the final refinement stages at calculated positions (C–H = 0.97 Å). At convergence 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}.

Results and Discussion

Description of the Structures

Salicylaldazine crystallizes in the monoclinic space group $P2_1/n$. Table 1 lists the crystallographic data and refinement parameters, Table 2 selected bond lengths and bond angles. The calculated values of the parameters for the optimized structure are given in italics. The calculated values are in reasonable agreement with the Xray structural data. The deviation between the two sets is assigned to the crystal field stabilization and intra and intermolecular hydrogen bonding effects. Figure 1 shows the Ortep view with atom numbering of the salicylaldazine, which was drawn using 25% probability ellipsoids.

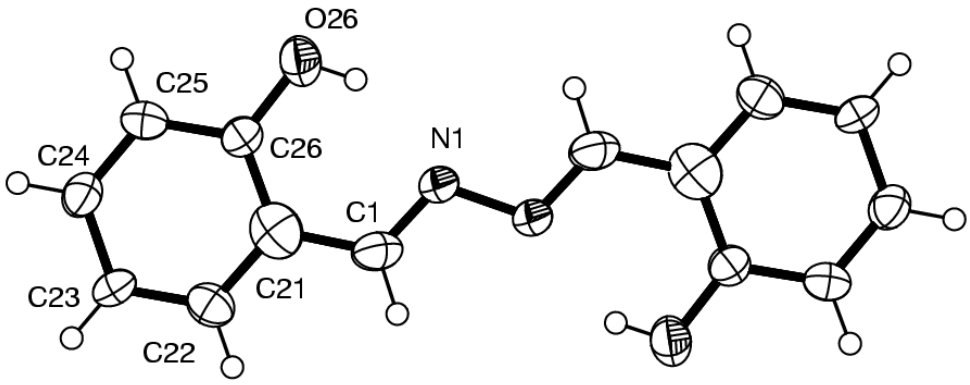


Fig. 1 Ortep view with atom numbering of the salicylaldazine, drawn using 25% probability ellipsoids.

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 H26—O26 and also N1_a and H26_a—O26_a.. In **5**, O26–H26 acts as a donor in the three-centre O26-H26···N1

interaction which is intramolecular in nature, and coplanar with the adjacent benzene ring [C1-N1-N1_a-C1_a : 179.98(12)^0, N1_a-N1-C1-C21 : 179.88(11)^0, N1-C1-C21-C22 : 179.54(12)^0, N1-C1-C21-C26 : 1.32(19)^0]. In a second hydrogen bond, O26 acts as an acceptor in a three-centre C1-H11$\cdots$O26 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 hydrogen bonds with aliphatic hydrogen atoms of two adjacent molecules, thus forming a polymeric and strongly hydrogen-bonded chain [C1-H1$\cdots$O26: 3.37(2) A and 167^0] (Table 3) along the a axis. There is no visible π-π interaction between such a chain and its two immediate neighbors, as the distance between neighboring benzene rings ~ 6.5 Å.

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

Empirical formula	C_7H_6NO
Formula weight	120.13
Colour, habit	Yellow ,
Crystal size /mm	0.66 x 0.51 x 0.61
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.554(3) Å α = 90 ^{0}
	b =6.338(2) Å β = 107.89 (2) ^{0}
	c =11.864(5) Å γ = 90 ^{0}
Volume /Å^3	612.0(4) Å^3
Z	4
Density(calcd)/Mg cm^{-3}	1.304
Absorption coefficient /mm^{-1}	0.089
F(000)	252
Diffractometer	
Temperature/K	293(2)
θ range for data collection	3.69 to 27..49
Limiting indices	-11< =h < =1,- < =h < = 1, -15 < =h < = 15,
Reflections collected /unique	1934 / 1383 , R (int) =0.0339
Completeness to theta =27.49	98.9 %
Refinement methode	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 σ(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	0.232 and -0.139 e Å^{-3}

Table 2 Selected bond lengths (Å) and angles (^{0})

N1-C1	1.284(2) / *1.307*	C21-C1-H11	119.3 / *113.6*
N1-N1_a	1.404(2) / *1.345*	C22-C21-C1	120.05(11) / *116.3*
C1-C21	1.454(2) / *1.462*	C26-C21-C1	121.59(11) / *125.6*
C26-O26	1.350(2) / *1.367*		
N1-C1-C21	121.40(1) / *123.0*		
N1-C1-H11	119.3 / *123.5*		
C1-N1-N1_a	113.51(1) / *118.7*		

Table 3 Hydrogen-bonding geometry (Å, ^{0})

D-H···A	D-H	H···A	D···A	D-H···A
O26-H26···N1	0.82 / *0.97*	1.89 / *2.095*	2.62(2) / *2.89*	147
C1-H1···O26^{b}	0.93	2.45	3.37(2)	167

Symmetry code: (a) 1-x, -y, -z (b) 1/2+x, 1/2+y, -1/2+z

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 double proton transfer 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 reaction, the N1—H26 distance has been considered as the reaction coordinate. For the intramolecular double proton transfer both N1—H26 ($R_{1\text{-}26}$) and N1_a—H26_a distances have been treated as reaction coordinates. However, considering the symmetric structure of the molecule, variation of both the distances have been kept same in each stage. Fig. 2 depicts the simulated PECs for the intramolecular single and double proton transfer processes of the isolated molecule in the S_0 and S_1 states. The figure clearly reveals that the tautomer formation through intramolecular single proton transfer (SPT) in the ground state leads to endothermicity ($\Delta H_{calc.}$ = 10.4 kcal mol^{-1}). However, the reaction becomes exothermic in the S_1 state ($\Delta H_{calc.}$ = – 9.2 kcal mol^{-1}). Thus, the SPT reaction is thermodynamically unfavorable in the ground state but it is 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 single proton transfer is feasible in the S_1 state although it is improbable in the ground state.

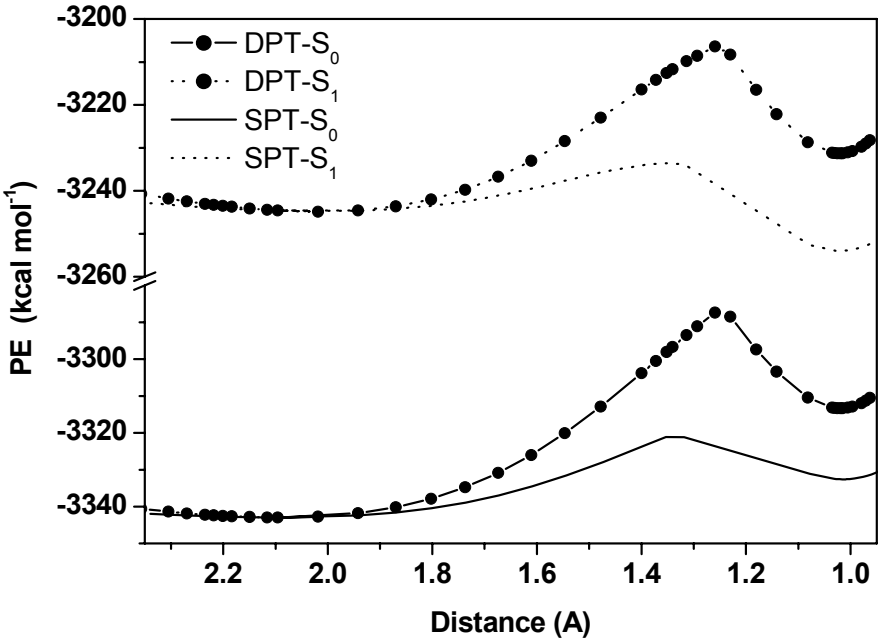


Fig.2 : Potential energy curves for the proton transfer process of salicylaldazine in S_0 and S_1 states. SPT and DPT represent single and double proton transfer respectively.

A similar treatment for the intramolecular double proton transfer (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 kcal mol^{-1} and 13.6 kcal mol^{-1} respectively. Although the endothermicity is reduced remarkably in the excited state, thermodynamics do not favor the IDPT process in either of the two states. The activation energies for the IDPT process are calculated to be 55.6 kcal mol^{-1} and 38.4 kcal mol^{-1} in the 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 simulate potential energy curves, thus, suggests that salicylaldazine is susceptible to excited state intramolecular single proton transfer but in spite of being symmetric the corresponding double proton transfer is unfavorable both from thermodynamic as well as kinetic point of view.

Acknowledgements

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