Crystal structure and geometry-optimization study of 2-benzyliminiomethylene-4-nitrophenolate

Biplab Mondal[a], Goutam Kumar Lahiri[a,*], Panče Naumov[b], Seik Weng Ng[c]

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India*
[b]*Institute of Chemistry, Sv. Kiril i Metodij University, P.O. Box 162, MK-1001 Skopje, Macedonia*
[c]*Institute of Postgraduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Abstract

5-Nitro-2-hydroxybenzaldehyde condenses with benzylamine to yield a Schiff base that exists in the solid state as zwitterionic form as 2-benzyliminiomethylene-4-nitrophenolate. In the crystal structure, two zwitterions are linked together as a centrosymmetric dimer by hydrogen bonds involving the iminium hydrogen atom [$N \cdots O_{intramonomer}$ = 2.653(2), $N \cdots O_{intradimer}$ = 2.880(2) Å]. Geometry-optimizations on the monomeric zwitterion and the isomeric hypothetical 2-benzyliminomethylene-4-nitrophenol molecule by the B3LYP/6-31++G(d,p) method imply an endothermic process [ΔH = 12.4 kcal mol^{-1}] for the transfer of the phenolic proton in the hypothetical neutral molecule to furnish the zwitterionic molecule.

Keywords: 2-Benzyliminiomethylene-4-nitrophenolate; Zwitterion; Crystal structure; Hydrogen bonding; Geometry-optimization

1. Introduction

The HO-2-C$_6$H$_4$CH=NR salicylideneimine Schiff bases behave as oxygen-donor ligands to Lewis-acidic organotin(IV) compounds as they coordinate to the tin ion through the phenolic oxygen atom. In the complexes, the phenolic hydrogen atom is shifted to the imino nitrogen atom which leads to the formation of an N−H···O unit [1]. The Schiff bases are neutral compounds, as are the saturated Schiff base HO-2-C$_6$H$_4$CH$_2$−NH−CH$_2$CH$_2$N(CH$_3$)$_2$ [2] and the bromo-substituted 4-Br-2-OH−C$_6$H$_4$CH$_2$−NH−CH$_2$CH$_2$-N(CH$_3$)$_2$ [3]. Interestingly, the replacement of the bromo substituent by the electron-withdrawing nitro group affords a saturated Schiff base that exists in the solid state as a zwitterion. The σ-donating phenolato-imine Schiff base, 2-benzyl-iminiomethylene-4-nitrophenolate, has been used in the synthesis of mixed ligand ruthenium−monoterpyridine/ruthenium-bis-bipyridine complexes in order to study the effect of the ancillary moiety on the redox and photophysical aspects of the ruthenium−terpyrine/bipyridine cores [4,5]. The crystal structure of the organic entity, 2-benzyliminiomethylene-4-nitrophenol, itself is now determined, and this is compared with the hypothetical isomer by using geometry optimization methods.

Table 1
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $C_6H_5CH_2N^+H=CH-4-NO_2-C_6H_3O^-$

Atom	x	y	z	U_{eq}
O1	0.7078(2)	0.4898(1)	0.6243(1)	0.052(1)
O2	1.6675(3)	0.4049(1)	0.9313(2)	0.094(1)
O3	1.6163(2)	0.3492(1)	0.7385(2)	0.081(1)
N1	1.5521(3)	0.3880(1)	0.8132(2)	0.063(1)
N2	0.6562(2)	0.4232(1)	0.3868(2)	0.041(1)
C1	0.9006(3)	0.4663(1)	0.6673(2)	0.041(1)
C2	1.0453(3)	0.4806(1)	0.8046(2)	0.050(1)
C3	1.2513(3)	0.4556(1)	0.8492(2)	0.052(1)
C4	1.3325(3)	0.4149(1)	0.7615(2)	0.046(1)
C5	1.2049(3)	0.3995(1)	0.6293(2)	0.044(1)
C6	0.9896(3)	0.4243(1)	0.5802(2)	0.038(1)
C7	0.8595(3)	0.4054(1)	0.4439(2)	0.043(1)
C8	0.5203(3)	0.4001(1)	0.2505(2)	0.046(1)
C9	0.3604(3)	0.3468(1)	0.2637(2)	0.045(1)
C10	0.1546(3)	0.3426(1)	0.1647(2)	0.059(1)
C11	0.0107(4)	0.2928(1)	0.1741(3)	0.080(1)
C12	0.0678(5)	0.2479(1)	0.2810(4)	0.089(1)
C13	0.2705(5)	0.2522(1)	0.3804(3)	0.082(1)
C14	0.4150(4)	0.3009(1)	0.3710(2)	0.061(1)

U_{eq} is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

2. Experimental

2.1. Synthesis

The Schiff base was synthesized by condensing 5-nitrosalicylaldehyde (0.17 g, 1 mmol) dissolved in ethanol (15 ml) and benzylamine (0.11 g, 1 mmol) at 0 °C. The solution was stirred at this temperature for 1 h; the yellowish orange product that separated was collected, washed with cold ethanol and then purified by recrystallization from ethanol. The compound was isolated in 85% yield [4,5].

2.2. Crystallography

The single crystals were grown by slow diffusion of a dichloromethane solution of the compound in hexane followed by slow evaporation. The X-ray diffraction measurements were carried out on a four-circle CAD4 diffractometer ($\lambda = 0.71073$ Å) with a yellow $0.40 \times 0.20 \times 0.20$ mm specimen of the Schiff base. The 2422 reflections were collected by ω-scans to $\theta = 25°$ ($-7 \leq h \leq 0$, $-24 \leq k \leq 0$, $-11 \leq l \leq 11$), and the raw data were processed [6] for solution by direct methods. Of the 2136 independent reflections ($R_{int} = 0.021$), 1368 satisfied the $I > 2\sigma(I)$ threshold. The structure was refined [7] on 177 parameters to $R_1 = 0.041$, $wR_2 = 0.104$ ($R_1 = 0.080$, $wR_2 = 0.112$ for all reflections). The final difference map did not show any large peaks/holes. The nitrogen-bonded hydrogen atom was located and refined; the other hydrogen atoms were generated geometrically. Atomic coordinates are
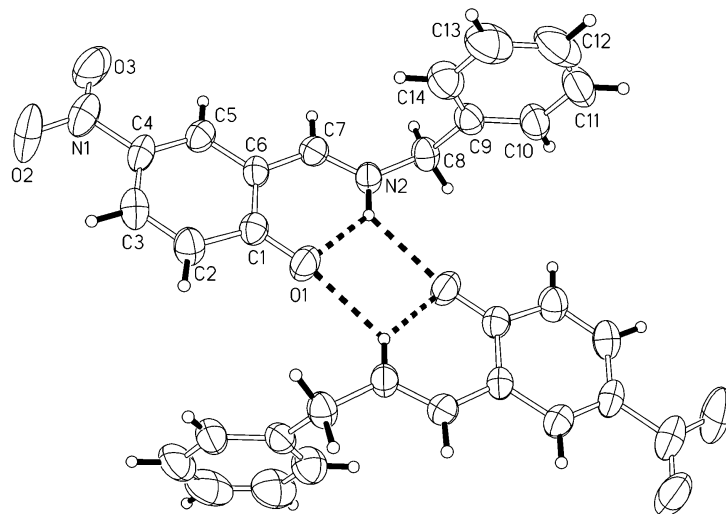

Fig. 1. *ORTEP* plot of the hydrogen bonded dimer at the 50% probability level. N2···O1 = 2.653(2), N2···O1i = 2.880(2) Å($i = 1 - x, 1 - y, 1 - z$).

Table 2
Bond lengths (Å) and angles (°) for $C_6H_5CH_2N^+H{=}CH\text{-}4\text{-}NO_2{-}C_6H_3O^-$ and the hypothetical $C_6H_5CH_2N{=}CH\text{-}4\text{-}NO_2{-}C_6H_3OH$

Bond dimension	$C_6H_5CH_2N^+H{=}CH\text{-}4\text{-}NO_2{-}C_6H_3O^-$ X-ray	$C_6H_5CH_2N{=}CH\text{-}4\text{-}NO_2{-}C_6H_3OH$ B3LYP/6-31++G(d,p) ab initio	
O1−C1	1.263(2)	1.263	1.351
O2−N1	1.235(2)	1.237	1.234
O3−N1	1.229(2)	1.239	1.234
N1−C4	1.442(2)	1.452	1.464
N2−C7	1.298(2)	1.316	1.273
N2−C8	1.453(2)	1.462	1.454
C1−C2	1.432(3)	1.447	1.401
C1−C6	1.442(2)	1.470	1.420
C2−C3	1.348(3)	1.368	1.388
C3−C4	1.402(3)	1.426	1.395
C4−C5	1.362(3)	1.377	1.391
C5−C6	1.400(2)	1.413	1.400
C6−C7	1.416(2)	1.411	1.474
C8−C9	1.513(3)	1.517	1.522
C9−C10	1.387(3)	1.399	1.401
C9−C14	1.381(3)	1.403	1.402
C10−C11	1.382(3)	1.398	1.398
C11−C12	1.364(4)	1.396	1.397
C12−C13	1.375(4)	1.399	1.397
C13−C14	1.368(3)	1.395	1.397
O2−N1−O3	122.8(2)	123.8	124.3
O2−N1−C4	118.4(2)	117.9	117.7
O3−N1−C4	118.8(2)	118.3	117.9
C7−N2−C8	124.0(2)	125.2	117.6
O1−C1−C2	122.2(2)	122.4	120.7
O1−C1−C6	121.9(2)	121.5	119.1
C2−C1−C6	115.9(2)	116.1	120.2
C1−C2−C3	121.7(2)	121.7	121.2
C2−C3−C4	120.8(2)	120.5	118.5
C3−C4−C5	120.8(2)	121.1	121.3
C3−C4−N1	119.5(2)	119.5	119.4
C5−C4−N1	119.7(2)	119.3	119.4
C4−C5−C6	119.8(2)	119.8	121.1
C5−C6−C1	121.0(2)	120.8	117.7
C5−C6−C7	118.2(2)	119.4	116.9
C7−C6−C1	120.8(2)	119.8	125.3
N2−C7−C6	124.7(2)	123.1	125.5
N2−C8−C9	112.3(2)	112.5	112.5
C8−C9−C10	119.8(2)	120.3	121.5
C8−C9−C14	121.7(2)	120.3	119.5
C10−C9−C14	118.5(2)	120.5	118.9
C9−C10−C11	120.0(2)	120.5	120.4
C10−C11−C12	120.7(2)	120.0	120.4
C11−C12−C13	119.8(2)	119.8	119.5
C12−C13−C14	120.0(3)	120.1	120.1
C13−C14−C9	121.2(2)	120.5	119.5
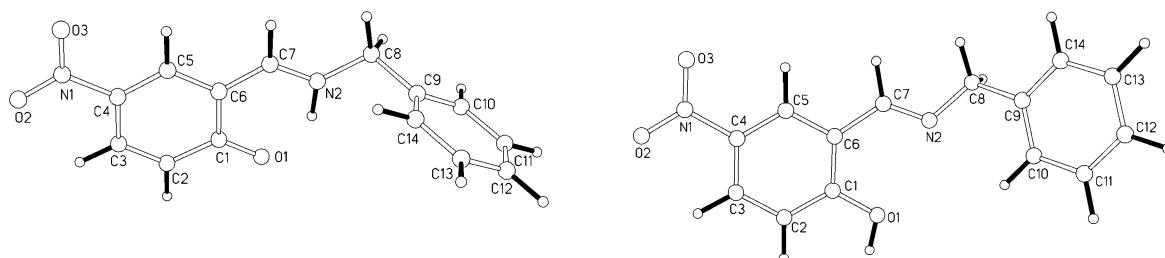
Fig. 2. Geometry-optimized structures for $C_6H_5CH_2N^+H=CH\text{-}4\text{-}NO_2\text{--}C_6H_3O^-$ (**1**) and $C_6H_5CH_2N=CH\text{-}4\text{-}NO_2\text{--}C_6H_3OH$ (**2**).

listed in Table 1, bond distances and angles in Table 2. The crystallographic-information-file is deposited with the Cambridge Crystallographic Data Center as CCDC 177554.

Crystal data: $C_6H_5CH_2N^+H=CH\text{-}4\text{-}NO_2\text{--}C_6H_3O^-$, $C_{14}H_{12}N_2O_3$, FW = 256.26, monoclinic, $P2_1/c$, $a = 6.3350(7)$, $b = 20.277(2)$, $c = 9.9304(7)$ Å, $\beta = 106.992(7)°$, $V = 1219.9(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.395$ g cm^{-3}, $\mu = 0.100$ mm^{-1}, $F(000) = 536$.

2.3. Geometry optimization

The potential minima of the monomeric models for $C_6H_5CH_2N^+H=CH\text{-}4\text{-}NO_2\text{--}C_6H_3O^-$ (**1**) and $C_6H_5CH_2N=CH\text{-}4\text{-}NO_2\text{--}C_6H_3OH$ (**2**) species isolated in vacuo were located by semi-empirical methods with *HyperChem* [8], and were subjected to further geometry optimization. With several initial guesses, both models featuring shallow potential landscapes and significant torsional freedom failed to converge by MM2, HF and DFT methods, particularly after extending the split basis set orbitals with diffuse functions necessary for treatment of the H-bonding. In order to get a better estimate of the relative stability, DFT single-point calculations were performed on the optimized structures in which a three-parameter exchange function [9] together with a correlation function [10] were used. The DFT minimum of the zwitterion (**1**) was located for an B3LYP/6-31++G(*d,p*) minimized structure of a B3LYP/6-31G refined AM1 output; the structure of (**2**) was then obtained by placing the dynamic proton near to the phenolato oxygen acceptor in the B3LYP/6-31G model and introducing an intramolecular bond between the phenol and imine functionalities. This action solely induced rotation of the

phenyl ring that was originally orthogonal to the nitrophenyl plane, with insignificant skeletal folding at the bridging nitrogen atom and the phenol proton away from the acceptor. As the energy of the neutral molecule is -875.8307 Hartrees and that of the zwitterion is -875.8504 Hartrees, the difference of 12k kcal mol^{-1} shows that the zwitterionic structure is the more stable of the two structures. The value was not adjusted for basis set effects, zero-point energy and other corrections. The calculations were performed with the GAUSSIAN-98W package [11].

1

2
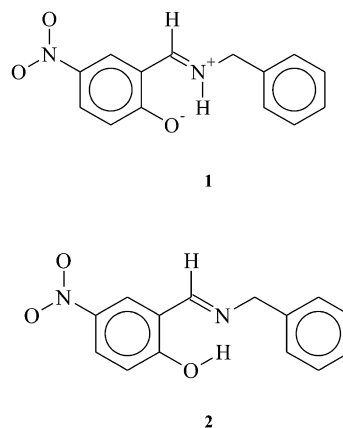
3. Results and discussion

2-Benzyliminiomethylene-4-nitrophenolate exists as a dimeric compound that is held together centrosymmetrically by hydrogen bonds [$N\cdots O_{intramonomer} = 2.653(2)$, $N\cdots O_{intradimer} = 2.880(2)$ Å] (Fig. 1). The crystal structure features an unusually short carbon–oxygen bond of

1.263(2) Å, which approximates distances found in carbonyl compounds such as aldehydes and ketones. This short distance implicates a quinonoid resonance contribution to the 4-nitrophenolato portion of the monomeric unit; the optimized structure shows that the distance is inherent for the electronic structure of the zwitterion and remains nearly uninfluenced by the three-centered hydrogen bond. The bond lengths in the aromatic system deviate from 1.39 Å, one being much shorter [C2–C3 = 1.348(3) Å] and one being much longer [C1–C6 = 1.442(2) Å] than this average. The nitro group that is in the *para* position is expected to shorten the carbon–oxygen bond; the distance is even shorter than that [1.295(3) Å] found in $(CH_3)_2NCH_2CH_2N^+H_2CH_2$-4-$NO_2$–$C_6H_3O^-$ [1]. The 2,4-dinitrophenolato ion in its morpholinium salt displays a bond distance of 1.282(3) Å [12] although it possesses two electron-withdrawing nitro groups.

In the geometry optimization calculations on the isolated zwitterion (**1**) and the hypothetical neutral molecule (**2**), the calculated bond dimensions (Table 2) agree better for the zwitterionic conformation (Fig. 2). In particular, all C–C values of both the rings in (**1**) are systematically overestimated, which can be attributed to method insufficiencies; nevertheless, these follow the quinonoid trend in the nitrophenyl portion of the experimental structure. For the isolated models, the proton transfer from (**1**) to such optimal neutral (**2**) is an endothermic process with $\Delta H = 12.4$ kcal mol^{-1} (B3LYP/6-31++G(d,p)). The barrier is probably altered in the crystal by the intramolecular and intermolecular bonding and the limited liberational freedom for phenyl rotation.

It should be noted that hydrogen bonding phenomenon has also been observed in solid 5-nitro-*N*-salicylideneethylamine [13].

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