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The *lp*–S–C–NH$^+$ stereoelectronic interaction and effect of hydrogen bonding on it

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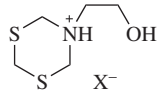
The stereoelectronic interaction in the S–C–NH$^+$ fragment and its manifestation in geometry of cations are considered using X-ray diffraction data and quantum-chemical calculations of 5-(2-hydroxyethyl)-1,3,5-dithiazinan-5-ium chloride and bromide.

Stereoelectronic interactions (SEI) play an important role in organic chemistry. In R–X–C–Y systems, where X is bearing a lone pair, and Y is more electronegative than carbon atom, they affect bond lengths, reactivity in S_N reactions and usually define conformational preferences.[1,2] The most widely accepted method for estimation of stereoelectronic interactions is based on second-order perturbation analysis of natural bond orbitals (NBO).[3] However, it has been shown recently that examination of SEI within the quantum theory of Atoms in Molecules (AIM)[4] provides significant supplement to NBO analysis. It recovers the anomeric effect by changes in energies and electron populations of atoms obtained by the integration of corresponding functions over atomic basins.[5,6] The applicability of AIM to this task was demonstrated for O–C–O and N–C–N systems. In our recent study, it was successfully applied to investigation of SEI in the N–C–S system in tetrahydro[1,3,4]thiadiazolo[3,4-*c*]-[1,3,4]thiadiazole.[7]



1a X = Br
1b X = Cl

In this work, we consider stereoelectronic interactions in the N–C–S system based on X-ray diffraction (XRD)† and quantum-chemical studies‡ of 5-(2-hydroxyethyl)-1,3,5-dithiazinan-5-ium bromide and chloride (**1a**,**b**).§ The major difference of these compounds from the previously studied system[7] is protonation of the nitrogen atom. The protonated nitrogen atom could not be involved in SEI as a donor due to absence of a lone pair but its acceptor abilities should increase. Thus, in this system, we could expect the appearance of *lp*–S–C–N stereoelectronic interactions being negligibly weak in the unprotonated *lp*–N–C–S system.[7] Note that the crystal structure of unprotonated 2-(1,3,5-dithiazinan-5-yl)-1-ethanol is already known.[15]

The XRD study of **1a** (see Figure 1) has shown that the six-membered ring has the conformation of distorted chair with N(1)–C(1)–S(1)–C(2) and N(1)–C(3)–S(2)–C(2) torsion angles of –61.7(2) and 63.0(2)°, respectively. This conformation is very favourable for *lp*–S–C–NH$^+$ stereoelectronic interactions, as the corresponding *lp*–S–C–N torsion angle in **1a** estimated based on the VSEPR theory[16] is close to 180°. Correspondingly,

† All measurements were performed with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans] at 100 K. Crystals of **1a** ($C_5H_{12}BrNOS_2$, M = 246.19) and **1b** ($C_5H_{12}ClNOS_2$, M = 201.73) are triclinic, space group $P\bar{1}$.

1a: a = 6.6491(8), b = 7.8313(10) and c = 8.9666(11) Å, α = 79.470(3)°, β = 88.684(4)°, γ = 81.142(2)°, V = 453.56(10) Å^3, Z = 2 (Z' = 1), d_{calc} = = 1.803 g cm^{-3}, μ(MoKα) = 4.930 cm^{-1}, F(000) = 248. 5906 measured reflections ($2\theta < 60°$), 2638 independent reflections (R_{int} = 0.0215), wR_2 = = 0.0527 and GOF = 1.002 for all independent reflections [R_1 = 0.0214 for 2383 observed reflections with $I > 2\sigma(I)$].

1b: a = 6.5384(6), b = 7.8098(7) and c = 8.8104(8) Å, α = 79.153(2)°, β = 89.298(4)°, γ = 79.406(2)°, V = 434.20(7) Å^3, Z = 2 (Z' = 1), d_{calc} = = 1.543 g cm^{-3}, μ(MoKα) = 0.856 cm^{-1}, F(000) = 212. 5622 measured reflections ($2\theta < 60°$), 2512 independent reflections (R_{int} = 0.0141), wR_2 = = 0.0774 and GOF = 1.006 for all independent reflections [R_1 = 0.0297 for 2374 observed reflections with $I > 2\sigma(I)$].

All calculations were performed using SHELXTL-Plus 5.0.[9]

CCDC 713877 and 713878 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

‡ *Ab initio* calculations were performed with the Gaussian03 program package[10] at B3LYP/6-311G*//B3LYP/6-311G* level. As convergence criteria, the extremely tight threshold limits of 2×10^{-6} and 6×10^{-6} a.u. were applied for the maximum force and displacement. To enhance DFT calculation accuracy the pruned (99.590) grid (keyword Grid=Ultrafine) has been used. The topological analysis of total electronic density and integration over atomic basins were performed using the AIMAll package.[11]

§ 2-(1,3,5-Dithiazinan-5-yl)-1-ethanol was synthesized as reported.[12,13]

5-(2-Hydroxyethyl)-1,3,5-dithiazinan-5-ium chloride **1b**. To a solution of the corresponding 2-(1,3,5-dithiazinan-5-yl)-1-ethanol (0.155 g, 1 mmol) in 5 ml of $CHCl_3$, under stirring, 37 wt% aqueous solution of HCl (0.083 ml, 1 mmol) and 5 ml of H_2O were added. The reaction mixture was stirred at 40–50 °C for 2 h. Aqueous layer was transferred to 10 ml beaker and left open for 3 days under room temperature until the volume of the solution reduced to 2 ml. Obtained precipitate was filtered to give 0.12 g of colorless crystals of **1** (63%), mp 142–144 °C (from water). Found (%): C, 29.56; H, 5.93; Cl, 17.32; N, 6.87; S, 31.55. Calc. for $C_5H_{12}ClNOS_2$ (%): C, 29.78; H, 5.96; Cl, 17.62; N, 6.95; S, 31.76.

5-(2-Hydroxyethyl)-1,3,5-dithiazinan-5-ium bromide **1a**. Colourless crystals of complex **2** were obtained in the same way. To a solution of 2-(1,3,5-dithiazinan-5-yl)-1-ethanol (0.115 g, 1 mmol) in 5 ml $CHCl_3$ 48 wt% aqueous solution of HBr (0.115 ml, 1 mmol) and 5 ml H_2O were added. Yield 0.09 g (51%), mp 166–168 °C (from water). Found (%): C, 29.60; H, 5.02; Br, 33.14; N, 5.63; S, 25.98. Calc. for $C_5H_{12}BrNOS_2$ (%): C, 29.39; H, 4.91; Br, 32.46; N, 5.69; S, 26.05.

Elemental analysis of C, H, N and S samples was performed on Karlo Erba, model 1106. Cl and Br contents were determined by Sheniger's method.[14] Melting points were determined on a Kofler unit.

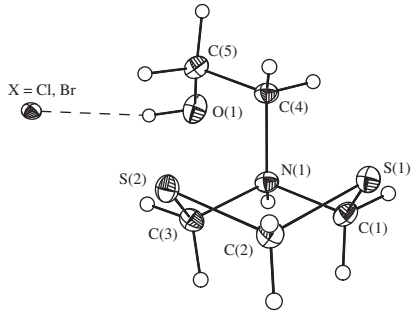


Figure 1 OH···X bonded cation **1** in a crystal. The atoms are represented by thermal ellipsoids (p = 50%).

the observed variations in bond lengths follow the expected increase of contribution of canonical structure S⁺=C···N. Indeed, the C(1)–S(1) and C(3)–S(2) [1.797(2) and 1.799(2) Å, respectively] bonds are shorter than S(1)–C(2) and S(2)–C(2) ones [1.806(2) Å], as they are strengthened due to SEI. Correspondingly, the weakened N(1)–C(1) and N(1)–C(3) bonds [1.514(2) and 1.510(2) Å, respectively] are elongated in respect to N(1)–C(4) [1.501(2) Å].

The variations of S–C bond lengths can possibly be a consequence of intermolecular interactions in a crystal of **1a**. The analysis of crystal packing in **1a** revealed that this crystal is formed by strong N⁺H···Br⁻ [N···Br 3.215(1) Å, ∠ N–H···Br 154(2)°] and OH···Br⁻ [O···Br 3.216(1) Å, O–H···Br 160(2)°] hydrogen bonds. Other intermolecular contacts in a crystal of **1a** are negligibly weak (see Online Supplementary Materials). The compound **1b** is isostructural† to **1a**, with the only notable difference occurring in hydrogen bond lengths. The observed shortening of the O–H···Cl⁻ [O···Cl 3.087(1) Å, O–H···Cl 163(2)°] and N–H···Cl⁻ [N···Cl 3.062(1) Å, N–H···Cl 152(2)°] hydrogen bonds in **1b**, as compared to **1a**, is explained by differences in chloride and bromide ionic van der Waals radii.

Thus, the observed variation in bond lengths cannot be explained by crystal packing. Moreover, they are in line with previously observed differences in C–S bond lengths of protonated 5-methyl-1,3,5-dithiazinane[17] (CCDC refcode ISUWEY). At the same time, the unprotonated 2-(1,3,5-dithiazinan-5-yl)-1-ethanol[17] (CCDC refcode ACAMIB) exhibits opposite tendencies in bond lengths: the S(1)–C(2) bond in it [1.803(3) Å] is significantly shorter than S(1)–C(1) one [1.840(3) Å] indicating strong *lp*–N–C–S stereoelectronic interactions.

To perform deeper investigation of SEI *lp*–S–C–NH⁺ and evaluate its energy, the B3LYP/6-311G* calculation of protonated 2-(1,3,5-dithiazinan-5-yl)-1-ethanol in gas phase was performed. The deviation of the calculated geometry for cation **1** in a gas phase from experimental was significant, with a maximum difference of 0.03 Å for the S(1)–C(2) bond. The tendencies in C–S and C–N bond lengths observed in a crystal became more pronounced in a gas phase, with difference between S(1)–C(1) and S(1)–C(2) bond lengths (1.831 and 1.806 Å, respectively) exceeding 0.02 Å. The analysis within the NBO scheme demonstrated the value of 9.9 kcal mol⁻¹ for $n_S \rightarrow \sigma^*_{C-N}$ interaction, thus indicating the presence of medium strength SEI. At the same time, the bond lengths indicate that this interaction in gas phase is significantly stronger than in crystal and the conclusions from gas-phase calculations cannot be directly applied to the structure observed in a crystal.

This fact can be explained by difference in hydrogen bonding of protonated nitrogen atom. Indeed, the protonated nitrogen atom in crystal is involved in a strong intermolecular NH⁺···Br⁻ hydrogen bond, while in isolated state it is only compensated by an intramolecular NH⁺···OH one. The topological analysis of total

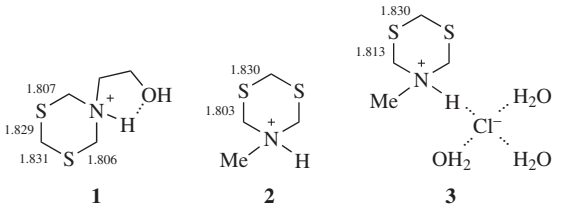


Figure 2 Model compounds **1**–**3**. The C–S bond lengths according to B3LYP/6-311G* calculation are given in Å.

electron density function $\rho(r)$ for this cation revealed the (3, –1) critical point corresponding to this interaction [$\rho(r)$ = 0.1755 eÅ^3, $\nabla^2\rho(r)$ = –0.699 eÅ^3] with an energy of 6.8 kcal mol⁻¹ according to the Espinosa–Lecomte correlation.[18] There are no experimental data available for energies of NH⁺···Br⁻ interactions in crystal, but the energy for NH⁺···Cl⁻ interactions is estimated at ~10 kcal mol⁻¹.[19] We can suggest that stronger H-bonding of a protonated nitrogen atom leads to greater charge transfer to nitrogen atom that decreases its acceptor ability and weakens the *lp*–S–C–NH⁺ stereoelectronic interaction.

To check our suggestion, the calculation of the structures of model compounds **2** and **3** in a gas phase was performed followed by the NBO analysis. Cation **2** was chosen as a model of cation **1** without hydrogen bonding, and complex **3** was calculated to analyse the changes in S–C–NH⁺ induced by stronger H-bonding. The results of calculation agree with suggestion that the strength of *lp*–S–C–N SEI is affected by the strength of N⁺–H···X bond.

Indeed, the C(2)–S(1) bond in **2** is by 0.004 Å shorter than that in **1**, and in complex **3** it is by 0.005 Å lengthened in comparison with **1** (see Figure 2). The changes in $n_S \rightarrow \sigma^*_{C-N}$ mixing energies follow the changes in C(2)–S(1) bond length: according to NBO data, the SEI is by 0.68 kcal mol⁻¹ stronger in **2** and by 1.07 kcal mol⁻¹ weaker in **3** in comparison with **1**.

The study of integral charges and energies in cations **1** and **2** has shown that the charge redistribution caused by hydrogen bonding has greater impact on integral atomic charges than the SEI in *lp*–S–C–N. As it was shown previously,[5–7] the SEI in *lp*–X–Y–Z increases the integral charges of atoms X and Z and decreases the charge of atom Y. Thus, the stronger SEI in **2**, in comparison with **1**, must be reflected in increase of positive charge on C(1) and C(3) atoms. Instead, the charge of carbon atoms in **2** was by 0.02e lower than that in **1**. This result can be explained on the basis of hydrogen bonding properties summarized by Koch and Popelier:[8] the N⁺–H···O hydrogen bonding leads to decrease of N(1) and O(1) charge, and the charge is transferred to these atoms from other atoms in the molecule.

Complex **3**, besides hydrogen bonding, was affected by charge transfer from Cl⁻. The chloride anion in this complex beared a charge of only –0.74e, with 0.14e transferred to cation and 0.04e to each water molecule. As a result, each carbon atom gained ~0.02e, and each sulfur atom gained more than 0.09e.

Thus, the analysis of both experimental and calculated bond lengths and NBO data supports the presence of *lp*–S–C–N interactions and shows that they are weakened by hydrogen bonding with the NH⁺ group. However, the effects of charge redistribution caused by hydrogen bonding have bigger impact on atomic properties than stereoelectronic interactions and thus the method proposed previously[7] cannot be applied to estimate the energy of these interactions.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.01.006.

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