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The role of H-bonds in charge transfer in the crystal of 1,5-naphthalenedisulfonic acid tetrahydrate

Konstantin A. Lyssenko,*[a] Petr Yu. Barzilovich,[b] Sergei M. Aldoshin,[b] Mikhail Yu. Antipin[a] and Yuri A. Dobrovolsky[b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*
[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russian Federation*

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Electron density analysis in the title compound has revealed that, due to H-bond formation, the total charges of the dianion and $H_5O_2^+$ cation are substantially decreased and bond length distribution in the SO_3 moiety can be directly related to the total energy of the cation–anion interactions and partial charges.

Aliphatic and aromatic sulfonic acids are well-known proton donation components for fuel cells.[1] A common and important characteristic of all these species is their involvement in hydrogen bonding. Clearly, the hydrogen atom transfer is directly related to the strengths of the hydrogen bonds and thus for understanding this phenomenon, in addition to structural data, it is desirable to obtain direct information on the nature of H-bonds, their energy and role in charge transfer from anions to cations.[1(b)] Although the X-ray diffraction data give all structural information, it is insufficient for estimation of the interaction energy due to cooperative effects of H-bonds in cation–anion associates.[2]

At the same time, this can be solved within the high-resolution X-ray diffraction (XRD) analysis, which makes it possible to obtain the total electron density function [$\rho(r)$] in crystal.[3] Consequent topological analysis of $\rho(r)$ in terms of Bader's 'Atoms in Molecule' (AIM) theory[4] allows one to fetch out all bonding interactions and even estimate their energy by means of Espinosa's correlation scheme.[5] Although the usage and accuracy of this approach for XRD investigation of H-bonds have been illustrated for various systems,[2,5,6] such an analysis for sulfonic acids was not performed.

In order to estimate the strength of H-bonds in sulfonic acids and their role in charge transfer in the solid state, we performed high resolution XRD analysis of 1,5-naphthalenedisulfonic acid **1**[†] that can be considered as a simple model system for proton donation components. Previously, the crystal structure of **1** was not described and the only available structural information was limited to solvate of **1** with DMF that crystallizes as salt with two oxonium cations.[7] In contrast, the crystals of **1** easily grown from aqueous solutions by slow evaporation at room temperature correspond to the salt with two Zundel-type ions ($H_5O_2^+$ cation) (Figure 1). Note that two different polymorphs of **1** with $H_5O_2^+$ cations were obtained depending on the concentration of **1**. In one of these polymorphs (**1A**), the dianion is located in general position while in the second (**1B**) it is lying in the centre of symmetry. The peculiarities of the geometry and supramolecular organization of **1A** and **1B** are similar. The crystal packing of both crystals can be described as alternating anionic layers, in which dianions are assembled *via* stacking interaction with a small area of ring overlap [the shortest C···C distances are 3.446(1) and 3.387(1) Å in **1A** and **1B**, respectively], and cationic layers composed from Zundel-type ions that interconnect the former by means of H-bonds into a 3D framework. The difference between crystal packings in **1A** and **1B** is reflected in some variation of cationic···anionic H-bond geometry (see Online Supplementary Materials) and in mutual disposition of a naphthalene ring in adjacent layers: skewed in **1A** and parallel in **1B** (see Online Supplementary Materials). Clearly, the S–O$^-$ or S=O bond lengths depend on the strengths of H-bonds, in which they participate. Thus assuming that SO_3 groups in **1A** and **1B** are characterized by almost the same S–O bond length distributions [1.4507(4)–1.4759(4) and 1.4554(4)–1.4791(4) Å] we can propose that despite of some H-bond strength variation charge transfer from cation to anion in **1A** and **1B** is merely the same (see Online Supplementary Materials). The same conclusion can be drawn from the analysis of $H_5O_2^+$ geometry. Indeed, the H_2O moieties in **1A** and **1B** characterized by perpendicular orientation are connected by asymmetric H-bond with O···O separation of 2.43 Å and difference of $H_2O···H···OH_2$ distances varying in the range of 0.41–0.54 Å. The unexpected feature of **1A** and **1B** is the disordering of its 'water component' (Figure 1). The ratio for two positions of water molecules in **1A** and **1B** is different and is likely to be temperature dependent. Indeed, in **1B** at 273 K, two components are characterized by self occupancy

[†] Crystals of **1** ($C_{10}H_6O_6S_2·2[H_5O_2]$, M = 360.35) are monoclinic, space group $P2_1/c$.

1A: at 100 K, a = 9.0690(4), b = 7.0547(3) and c = 22.938(1) Å, β = = 95.5424(7)°, V = 1460.7(1) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.639 g cm^{-3}, μ(MoKα) = 4.15 cm^{-1}; 134740 reflections were measured; $2\theta < 95°$; 13338 independent reflections; wR_2 = 0.0736 and GOF = 1.009 (for all independent reflections), R_1 = 0.0260 [for 11301 observed reflections with $I > 2\sigma(I)$].

1B: at 273 K, a = 11.3930(4), b = 9.0358(3) and c = 7.1846(3) Å, β = = 100.326(2)°, V = 727.64(5) Å^3, Z = 2 (Z' = 0.5), d_{calc} = 1.645 g cm^{-3}, μ(MoKα) = 4.16 cm^{-1}; 42606 reflections were measured; $2\theta < 100°$; 7575 independent reflections; wR_2 = 0.0948 and GOF = 1.042 (for all independent reflections), R_1 = 0.0323 [for 5403 observed reflections with $I > 2\sigma(I)$]. At 100 K, a = 11.2926(3), b = 8.9826(2) and c = 7.1552(2) Å, β = 99.970(1)°, V = 714.84(3) Å^3, Z = 2 (Z' = 0.5), d_{calc} = 1.674 g cm^{-3}, μ(MoKα) = 4.24 cm^{-1}; 21714 reflections were measured; $2\theta < 100°$; 6919 independent reflections; wR_2 = 0.1346 and GOF = 0.975 (for all independent reflections), R_1 = 0.0371 [for 5896 observed reflections with $I > 2\sigma(I)$].

CCDC 706180–706182 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, 2008.

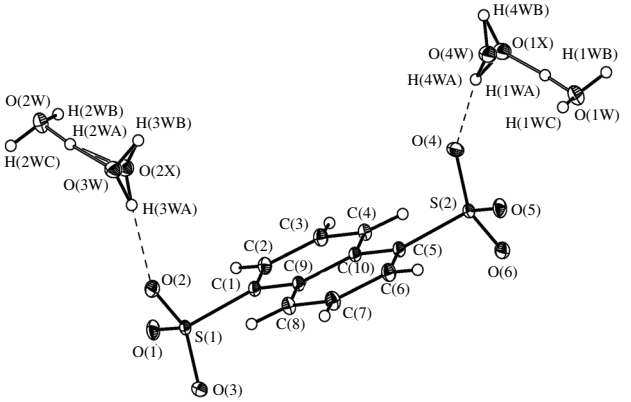

Figure 1 The general view of **1A** in presentation of atoms by thermal ellipsoids ($p = 50\%$). Atoms O(1X) and O(2X) correspond to the minor component for atoms O(3W) and O(4W) with occupancies equal to 0.04. Selected bond lengths in **1A** (Å): S(1)–O(3) 1.4547(4), S(1)–O(1) 1.4611(4), S(1)–O(2) 1.4768(4), S(1)–C(1) 1.7692(4), S(2)–O(4) 1.4554(4), S(2)–O(5) 1.4581(4), S(2)–O(6) 1.4791(4), S(2)–C(5) 1.7704(4), O(1W)···O(4W) 2.4371(8), O(2W)···O(3W) 2.4393(8) and in **1B**: S(1)–O(1) 1.4507(4), S(1)–O(3) 1.4579(4), S(1)–O(2) 1.4759(4), S(1)–C(1) 1.7703(5), O(1W)···O(2W′) 2.449(1).

factors (s.o.f.) of 0.60 and 0.40, while at 100 K the s.o.f. are 0.75 and 0.25. In turn, in case of **1A**, for which data collection has been carried out only at 100 K, the s.o.f. for minor component is as small as 0.04 and was localized only with the inclusion into the refinement of high-order reflections with $2\theta > 60°$. Note that such a type of disorder is not the unique feature of **1** and was also reported for 2,6-dihydroxy-3-methoxy-carbonyl-4-methylbenzenesulfonate oxonium trihydrate.[8] Assuming that routine XRD data can be insufficient for correct description of the $H_5O_2^+$ cation, we can not exclude that such a disorder is more frequently observed as it is accepted and can play an important role in the dynamics of proton transfer within the $H_5O_2^+$ ion.

Taking into account that disorder in **1A** at 100 K was negligible, we have carried out the multipole refinement[‡] and consequent topological analysis for analytical $\rho(r)$ function thus obtained. Despite of this disorder the accuracy of electron density distribution for all atoms with the only exception of O(4W) and O(3W) was acceptable. First, the deformation electron density (DED) maps for anion (see Online Supplementary Materials) and, especially, for Zundel-type ions are characterized by the expected features, namely, the hydrogen atom is directed towards highly polarized electron lone pair (Lp) of oxygen (Figure 2). Although the DED distributions for O–H···O–S type hydrogen bonds are similar, the degree of Lp polarization is significantly smaller (Figure 3). Furthermore, in addition to qualitative DED maps, such quantitative parameters as so-called

[‡] The multipole refinement of **1A** at 100 K was carried out within the Hansen–Coppens formalism[11] using the XD program package.[12] The refinement was carried out against F and converged to $R = 0.0183$, $Rw = 0.0212$ and GOF = 1.2013 for 10281 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria (the maximum difference of the mean square displacement amplitudes was 9×10^{-4} Å^2). The level of multipole expansion was octupole for all non-hydrogen atoms. The dipole D_{10} and the hexadecapoles H_{40} were refined for all hydrogen atoms for more accurate description of hydrogen bonds. The residual electron density was no more than 0.26 eÅ^{-3}. Topological analysis of the experimental $\rho(r)$ function was carried out using the WINXPRO program package.[13] The estimation of the kinetic energy $[g(r)]$ was based on the Kirzhnits approximation[14] relating it with values of the $\rho(r)$ and its derivatives: $g(r) = (3/10)(3\pi^2)^{2/3}[\rho(r)]^{5/3} + (1/72)|\nabla\rho(r)|^2/\rho(r) + 1/6\nabla^2\rho(r)]$. The usage of this relationship in conjunction with the virial theorem $[2g(r) + v(r) = 1/4\nabla^2\rho(r)]$ provided the value of potential energy density $[v(r)]$ in the critical points from experimental diffraction data.

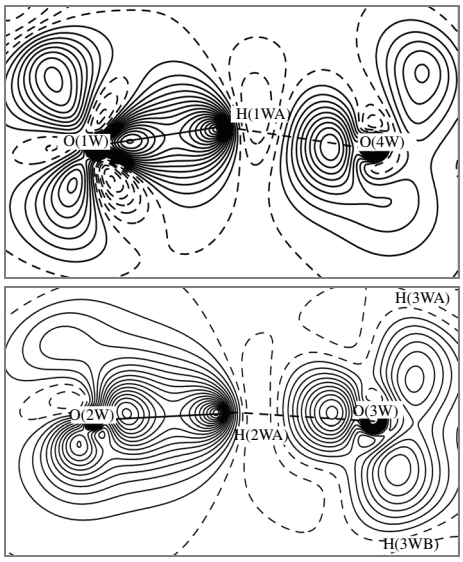

Figure 2 DED maps for Zundel ions in **1A**. The contours here and below are drawn with a 0.05 eÅ^{-3} step; the negative contours are dashed.

Hirshfeld test for anisotropic displacement parameters (no more than 9×10^{-4} Å^2), and mainly the values of Lagrangian $[-1/4\nabla^2\rho(r)]$ (no more than 4×10^{-4} a.u.) integrated within subspaces surrounded by atomic surfaces (that is atom according to AIM theory[4]) satisfy the reasonable threshold for each. Finally, the topological parameters for dianion (see Online Supplementary Materials) and, what is more important, for cation are reasonable. In particular, the topological parameters obtained for O–H···O bonds in model clusters of $[(H_5O_2)Cl_4]^{3-}$, in which the O···O distance (2.453 Å)[9] is close to those obtained in **1A**, are similar to each other. Indeed, the values of $\rho(r)$ and electron energy density $[h_e(r)]$ in the critical point (3, –1) of O(4W)···H(1WA) and O(3W)···H(3WA) bonds for above model and for cation in **1A** are 0.741 eÅ^{-3} and –0.0503 a.u. and 0.87–0.88 eÅ^{-3} and –0.0506 to –0.04853 a.u., respectively. Thus, we can conclude that analytical $\rho(r)$ function despite of disorder gave rather accurate values even for $H_5O_2^+$ cation, and we can use it to analyze the energy and charge distribution in a crystal of **1A**. Despite of 'central H-bond' asymmetry, it corresponds to an intermediate type of interatomic interactions that is common for so-called low barrier H-bonds.[6]

As it was mentioned above, in the crystal of **1A**, one can fetch out anion–anion and cation–anion type of interactions.

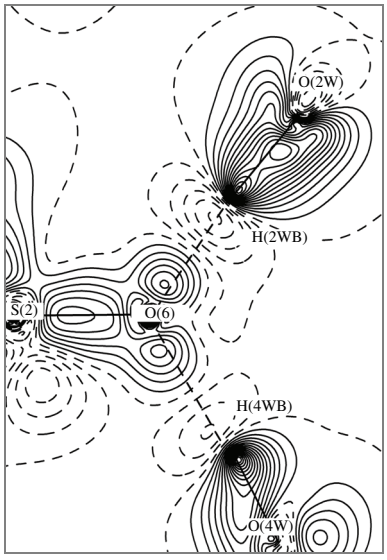

Figure 3 DED map illustrating the cation···anion H-bonds in **1A**.

Indeed, the critical point search has revealed that both of these types of contacts correspond to bonding interactions. Both the anion–anion binding represented by the stacking interactions [four independent contacts with $\rho(r)$ values in CP (3, –1) of *ca.* 0.04 eÅ^{-3}, E_{cont} = 0.8 kcal mol^{-1}] and C–H···O interactions [six independent contacts with $\rho(r)$ values of 0.02–0.08 eÅ^{-3}, E_{cont} = 0.4–2.4 kcal mol^{-1}] correspond to closed-shell type. Although the cation–anion interactions are significantly shorter and characterized by $\rho(r)$ values in CP (3, –1) as much as 0.14–0.25 eÅ^{-3} they do not correspond to intermediate type interactions as H-bond in $H_5O_2^+$, but are of closed-shell type [the $h_e(r)$ values are in the range of 0.004632–0.01229 a.u.]. The energy of H-bonds varies from 8.1 (O···O 2.686 Å) to 14.6 kcal mol^{-1} (O···O 2.598 Å) (see Online Supplementary Materials).

The high H-bond energy allows us to assume that due the cation–anion interactions the charges of two Zundel ion and sulfate anion must to some extent be equalized. Indeed, the integration of $\rho(r)$ leading to the charges for dianion has revealed that the total charge is –0.30e (see Online Supplementary Materials). Taking into account that charge leakage upon electron density integration is no higher than 0.05e, we can estimate charge transfer from the dianion to cations at 1.70±0.05e. Although this value seems to be large, if we take into account that each SO_3 group participates in at least four strong H-bonds, obtain that each of H-bonds leads to charge transfer that amounts to 0.21(5)e. For comparison, we can use values obtained by means of experimental analysis of $\rho(r)$ function in hydroxylammonium chloride[10(*a*)] and urea nitrate,[10(*b*)] as well as theoretical estimation for the closed-ion pair of guanidinium chloride.[10(*c*)] In these three systems, the charge transfer and corresponding total energy of cation–anion interactions are 0.72e for 45.2 kcal mol^{-1},[10(*a*)] 0.53e for 46.8 kcal mol^{-1} [10(*b*)] and 0.22e for 9.8 kcal mol^{-1},[10(*c*)] respectively. Taking into account that the energy of all H-bonds in **1A** is 92.6 kcal mol^{-1}, the estimated energy transfer is rather reasonable.

It should be noted that the values of H-bond energy well correlate with the charges of oxygen atoms. Indeed, the O(2) and O(6) atoms, which form two strong H-bonds with total energies of 21 and 26.1 kcal mol^{-1}, are characterized by a charge of –0.85, while all other atoms that participate only in one strong H-bond are more negatively charged [–1.02(5) to –0.95(5)e]. Taking into account that the above variation of charge is in agreement with elongation of S–O bond for O(2) and O(6) atoms, it was intriguing to find the interconnection of total charges and energy of interactions with bond lengths distribution in SO_3 groups. First, the partial charge of SO_3 group [–0.45(5), –0.51(5)e] and the total energy of cation–anion (51.0, 51.4 kcal mol^{-1}) interactions for two independent moieties are merely the same. Furthermore, such parameters as the sum of S–O bond lengths are also equal [4.3926(4) Å] for S(1)O(1)O(2)O(3) and S(2)O(4)O(5)O(6) groups, and this clearly shows that the latter parameter that can be readily obtained even from routine X-ray diffraction data can serve as certain estimation of charge transfer in the sulfonic acid salt.

Therefore, the electron density analysis in the crystal of **1** has revealed that due to H-bonds between Zundel-type ions and SO_3 groups the charges in two moieties are significantly equalized and thus classification of them as cation and anion is substantially artificial. Taking into account that high-resolution X-ray diffraction data cannot be readily obtained for every crystal structure the further investigation will probably make it possible to check and develop the correlation scheme interconnecting S–O bond lengths with charge on it. The latter clearly is of great importance for the design of proton donation components.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.11.008.

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