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Experimental evidence of 3-centre, 2-electron covalent bond character of the central O-H-O fragment on the Zundel cation in crystals of Zundel nitranilate tetrahydrate

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Biserka Kojić-Prodić^a

Charge density of the Zundel cation in the crystal of $2[\text{H}_5\text{O}_2]^+[\text{C}_6\text{O}_8\text{N}_2]^{4-}\cdot 4\text{H}_2\text{O}$, is studied by X-ray diffraction and periodic DFT calculations. Covalent nature of the central O-H-O bonds in the Zundel cation is revealed: electron density at the two O-H critical points is about $1.0 \text{ e}\text{\AA}^{-3}$, corresponding to a three-centre, two-electron system. Bond orders derived from topology of electron density are 0.27 - 0.41, more similar to single O-H bonds (bond order 0.45 - 0.51) than $\text{H}\cdots\text{O}$ hydrogen bonds (bond orders 0.05 - 0.10).

Proton transfer is an ubiquitous phenomenon occurring in a vast majority of chemical reactions in aqueous media, including the most important biological processes.¹⁻⁴ The basic step in a variety of processes, ranging from enzyme catalysis³ to electric conductivity *via* the Grotthuss mechanism^{1,5}, is migration of a hydrogen cation (i.e. a proton) between two water molecules and it involves two well-known solvated forms: Eigen cation $[\text{H}_3\text{O}(\text{H}_2\text{O})_3]^+$ ⁶ and Zundel cation $(\text{H}_5\text{O}_2)^+$, which may also be denoted as $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ ⁷. However, after more than eight decades of intensive research^{2,8-11} this very basic chemical reaction still remains fundamentally unexplained. It is generally accepted nowadays that the Zundel cation is a stable chemical species, rather than a transition state of a proton migration¹², however its relation to the Eigen cation is still quite a mystery. It is even unknown which one is actually more stable¹³, and quantum chemical calculations still do not provide an unambiguous answer, invariant of the method and basis set used^{9,14}. It is well-known that the $\text{O}\cdots\text{O}$ distance in the Zundel cation is 2.40 - 2.45 Å, corresponding to a borderline case between a strong hydrogen bond and a weak (two-electron, three-centre) covalent bond. According to a simple model, $\text{O}\cdots\text{H}$ bonds have an order of 0.5¹⁰.

Our study, which combined variable-temperature X-ray diffraction, solid-state NMR and IR spectroscopies and *ab initio* calculations, has shown that the $\text{O}\cdots\text{O}$ distance is temperature invariant¹⁵, which is consistent with the covalent character of the $\text{O}-\text{H}^+-\text{O}$ bonds. These results also support a single-well potential with large-amplitude motion of the proton, rather than a statistically averaged proton hopping or tunnelling¹⁵. However, the issue of the proton migration is still ambiguous^{9,14}, and the study of the Zundel cation still poses a considerable experimental and theoretical challenge.

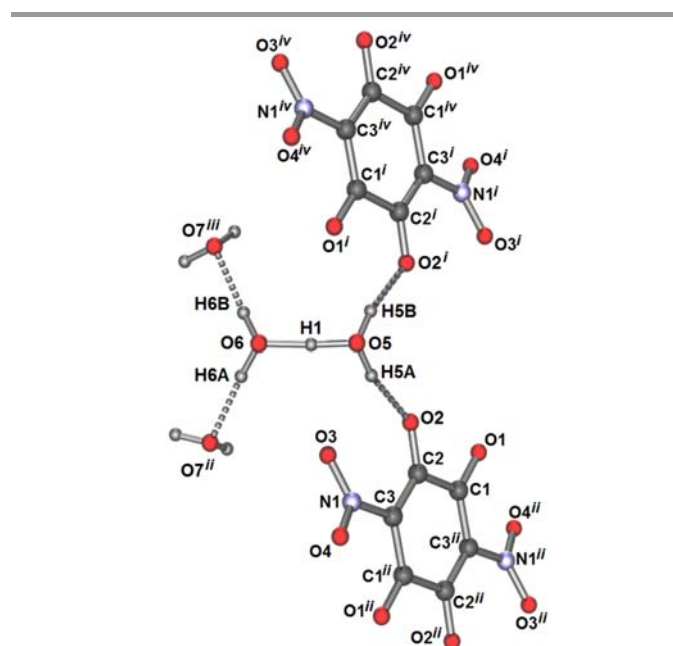


Figure 1 Environment of the Zundel cation with atom numbering scheme. Symmetry operators: *i*) $-x, 1-y, -z$; *ii*) $-x, 1-y, 1-z$; *iii*) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; *iv*) $x, y, 1-z$.

Zundel-like states trapped in crystals offer plenty of possibilities for the study of proton transfer. Crystal structure determination provides a time-averaged picture which then serves as a foundation for study of proton dynamics by spectroscopic (especially IR and solid-state NMR) and theoretical methods (post Hartree-Fock for discrete clusters and periodic DFT for simulation of crystal structure)^{15,16}. X-ray charge density studies of two systems involving a Zundel cation have been published recently: 1,8-bis(dimethylamino)naphthalene hydrochloride hydrate¹⁷ has a symmetric Zundel ion located on an inversion centre while the 1,5-naphthalenedisulfonic acid tetrahydrate¹⁸ compound has a highly asymmetric Zundel-like ion (the difference between two O-H bond lengths is about 0.5 Å) located in a general position. The present study involves nitranilic acid,¹⁹ a much smaller molecule and comprising no heavy atoms, allowing a more reliable modelling of low electron density around weakly diffracting hydrogen atoms.[‡]

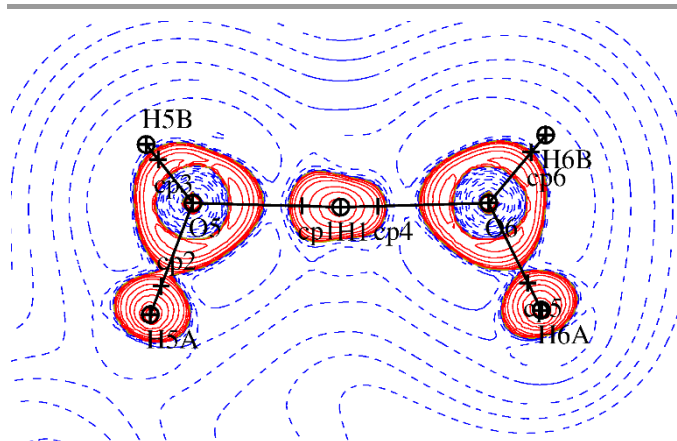


Figure 2 Laplacian of electron density of the Zundel cation in the plane defined by atoms O5, O6 and H6A. Positive density is shown in blue and negative in red; yellow dotted lines represent zero density.

The environment of the Zundel cation is shown in Fig. 1. It is located in a general position, and is slightly asymmetric due to an asymmetric environment. Its total charge, derived from the multipolar electron density, is $P_{\text{val}} = +0.86$ (Table 1), which is in good agreement with the formal value of +1. In terms of electron density, it can be treated as a single molecule, rather than two water molecules joined by hydrogen bonds: the two O-H bonds in O5-H1-O6 fragment are qualitatively similar to covalent bonds. Deformation density in both bonds is similar (Fig. 2), however the proton is located slightly closer to O5 (anionic side). The critical point (CP) electron density in the stronger O5-H1 bond is $\rho_{\text{cp}} = 1.13 \text{ e}\text{\AA}^{-3}$ and in the weaker O6-H1 bond $\rho_{\text{cp}} = 0.95 \text{ e}\text{\AA}^{-3}$, while in regular single O-H bonds it exceeds $2.0 \text{ e}\text{\AA}^{-3}$ (Table 2); these values are close to those reported by Woźniak *et al.*¹⁷. Also, both O6-H1 and O5-H1 bonds have a negative Laplacian $\nabla^2 \rho_{\text{cp}}$ value (Table 2), indicating a substantially covalent character. The corresponding topological bond orders are 0.26 and 0.33 for H1-O6 and H1-O5 bonds, respectively (Table 2)⁸, which is in agreement with calculated Cioslowski-Mixon bond orders²⁰ in short, strong hydrogen bonds.²¹ Single O-H bonds in water molecules are considerably stronger, with bond orders between 0.45 and 0.47 (Table 2), also in good agreement to calculated values (0.45 - 0.58).²¹ In H...O hydrogen bonds, maximum electron density is typically about $0.20 \text{ e}\text{\AA}^{-3}$ ²², Laplacians are positive and the corresponding bond orders are lower than 0.1. Therefore, we can conclude that the proton in the Zundel cation forms two weak covalent bonds (in fact a three-centre two-electron covalent bond), which are by an order of a magnitude stronger than common hydrogen bonding between water molecules.

The map of electrostatic potential (Fig. 3) reveals electron-rich areas around the oxygen lone pairs and electron-poor areas around the hydrogen atoms. On the other hand, the most positive potential on the density isosurface is located close to the central H1 proton. A slight asymmetry, generated by its environment, can be noted: the oxygen atom close to the nitranilate anions (O5) has a more negative charge than O6, which is interacting with the two water molecules (Fig. 3).

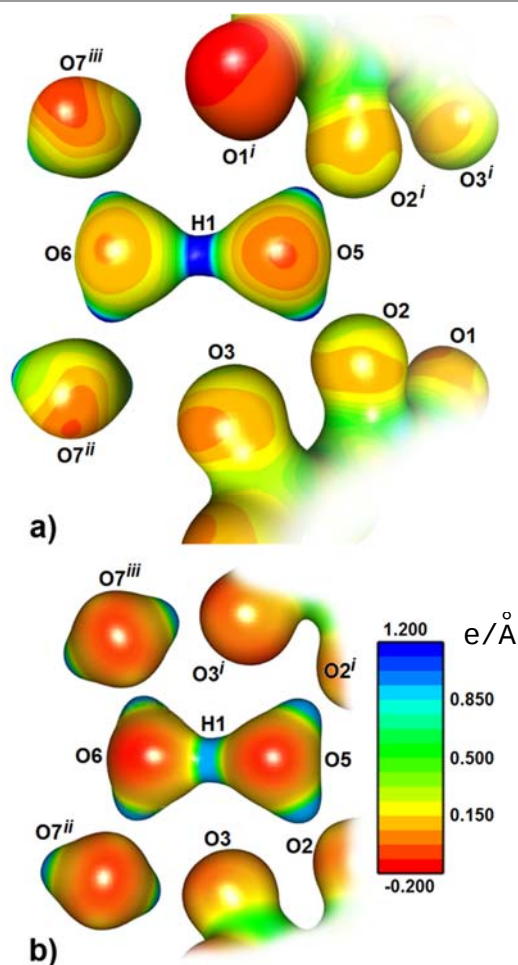


Figure 3 Electrostatic potential generated by a Zundel cation and its first coordination shell mapped on an electron density surface of $0.5 \text{ e}\text{\AA}^{-3}$: a) experimental, b) theoretical. Orientation is the same as in Fig. 1. Evident is greater concentration of the negative charge on the oxygen close to nitranilate dianions (right side). Symmetry operators: i) $-x, 1-y, -z$; ii) $-x, 1-y, 1-z$; iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Conclusions

Both central O-H bonds in the Zundel cation are weaker than common single bonds, but by an order of magnitude stronger than common hydrogen bonds. Therefore, the Zundel cation can be regarded as a single molecular species, rather than a hydrogen bonded cluster, and the central O-H-O fragment in fact represents a 3-centre, 2-electron bond.

In the studied system, due to asymmetric environment, the central proton is located slightly off midpoint of the O...O line, therefore the two O-H bonds are not equally strong. While the stronger one is considerably weakened compared to "pure" single bonds, the weaker one is, according to electron density and topological parameters, its bond order is approximately half of that of a "pure" single one.

Table 1 Atom charges (e) from the multipolar model. P_{val} derived values are from the $Q = N_{\text{val}} - P_{\text{val}}$ difference between number of valence electrons in neutral and refined multipolar atom. Esd's were obtained after refinement vs. all variables. Fitted charges were obtained with VMOPro software from the electrostatic potential in a layer 2.5 Å thick around the van der Waals surface of each moiety.

Atom	$N_{\text{val}}-P_{\text{val}}$	Bader	Fitted
O1	-0.36(1)	-1.11	-0.42
O2	-0.37(1)	-1.07	-0.47
O3	+0.05(1)	-0.23	-0.19
O4	+0.05(1)	-0.23	-0.20
N1	-0.27(1)	-0.18	+0.20
C1	+0.16(1)	0.66	+0.18
C2	+0.16(1)	0.58	+0.17
C3	-0.35(1)	-0.05	-0.19
total NA^{2-}	-1.86	-1.82	-1.84
O5	-0.53(1)	-1.17	-0.72
O6	-0.54(1)	-1.11	-0.63
H1	+0.33(1)	+0.70	+0.44
H5A	+0.40(1)	+0.60	+0.46
H5B	+0.40(1)	+0.61	+0.44
H6A	+0.40(1)	+0.61	+0.43
H6B	+0.40(1)	+0.61	+0.43
total cation	+0.86	+0.85	+0.86
O7	-0.68(1)	-1.23	-0.77
H7A	+0.38(1)	+0.65	+0.41
H7B	+0.38(1)	+0.65	+0.42
total water	+0.08	+0.07	+0.07

Correlations: $P_{\text{val}}*\text{Bader} = 0.80$; $\text{Bader}*\text{Fit} = 0.88$; $P_{\text{val}}*\text{Fit} = 0.86$

Table 2 Topology of electron density of O-H bonds in the Zundel cation, derived from experimental electron-density after multipole refinement. Electron density in the crystal water O7 and hydrogen bond O6-H6A...O7ⁱ are given for comparison. Symmetry operator: *i*) -x, 1-y, 1-z.

Bond	Length (Å)	Electron Density ($\text{e}\text{\AA}^{-3}$) ρ_{cp}	Laplacian ($\text{e}\text{\AA}^{-3}$) $\nabla^2\rho_{\text{cp}}$	Ellipticity	Bond order n_{topo}
O5-H1	1.220(2)	1.136	-10.0	0.00	0.33
O6-H1	1.222(2)	0.950	-4.32	0.01	0.26
O5-H5A	0.983	2.022	-23.1	0.01	0.44
O5-H5B	0.983	2.009	-22.2	0.00	0.44
O6-H6A	0.983	2.038	-22.8	0.02	0.45
O6-H6B	0.983	2.011	-21.8	0.02	0.44
O7-H7A	0.983	2.062	-31.7	0.01	0.47
O7-H7B	0.983	2.071	-31.4	0.00	0.47
H6A-O7 ⁱ	1.76(4)	0.212	3.65	0.02	0.07

Notes and references

‡ X-ray diffraction measurements were performed on a Bruker D8 Venture diffractometer at 100(2) K using MoK α radiation, to the maximum resolution of 0.50 Å. Atomic coordinates were taken from the room-temperature structure¹⁵ and multipolar refinement was carried out vs. all reflections F^2*2 up to $s = 0.9 \text{ \AA}^{-1}$ with program package *MoPro*.²³ To correct for thermal diffuse scattering,²⁴ a polynomial scale factor (monotonous increasing function of $s = \sin\theta/\lambda$) was refined and applied ($K = 0.06083 + 0.00771 s^4$). The lengths of the O-H bonds in water and Zundel molecules were restrained to 0.983(2) Å. The thermal motion of the hydrogen atoms were modelled as anisotropic, their ADPs being constrained to values calculated by the SHADE3 server²⁵.

The intramolecular motion was obtained from a lattice-dynamical model derived from periodic DFT calculations, whereas the external modes were obtained by a riding-approximation to the nearest oxygen atom. Dipoles were used to model deformation from sphericity. The Zundel proton H1, was refined with no distance restraints and was modelled with one dipole and one quadrupole directed towards O5 atom.

§ Topological bond orders were calculated using the fitted formula²⁶ $n_{\text{topo}} = a + b \lambda_3 + c (\lambda_1 + \lambda_2) + d \rho_{\text{cp}}$, with parameters a , b , c and d taken from literature.^{21,27}

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