Extremely short halogen bond: the nature and energy of iodine–oxygen interactions in crystalline iodic acid

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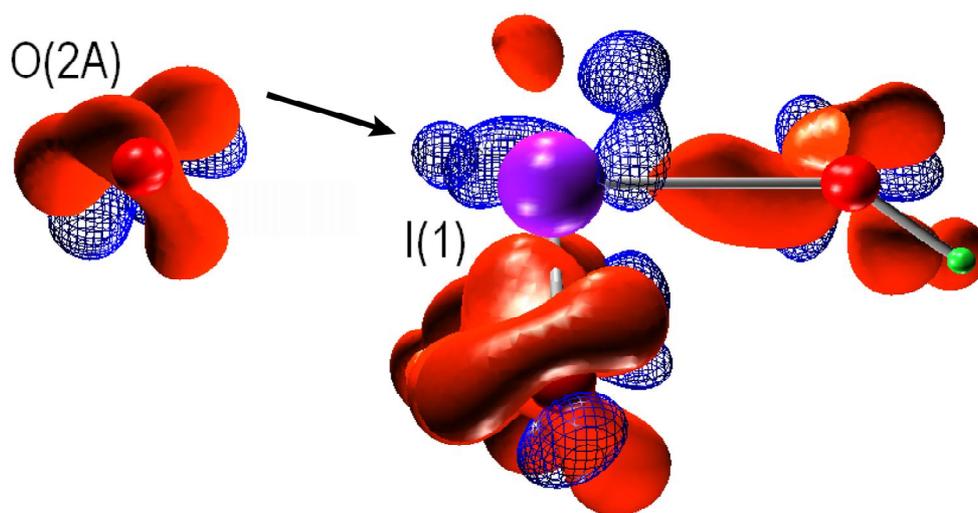

Figure S1 The 3D-distribution of DED in the section of the I…O interactions in α-HIO$_3$. Isosurface of DED equal to 0.25 eÅ^{-3} is shown by red; the negative isosurface (DED is –0.35 eÅ^{-3}) is shown by wireframe.

Note that the bond ellipticities (ε), which serve as measures of the π component, indicate the partial double-bond character of the I(1)−O(1) and I(1)−O(3) bonds (ε = 0.29 – 0.30). On the same basis, the I(1) −O(2) bond – its oxygen atoms is involved in the hypercoordinate I…O and H-bond – was found to be almost single one (ε = 0.12); the latter resembles the character of the chemical bonding observed for the chlorate anion in NaClO$_3$ [Yu. V. Nelyubina, K. A. Lyssenko, R. G. Kostyanovsky, D. A. Bakulin and M. Yu. Antipin, *Mendeleev Commun.*, 2008, **18**, 29].
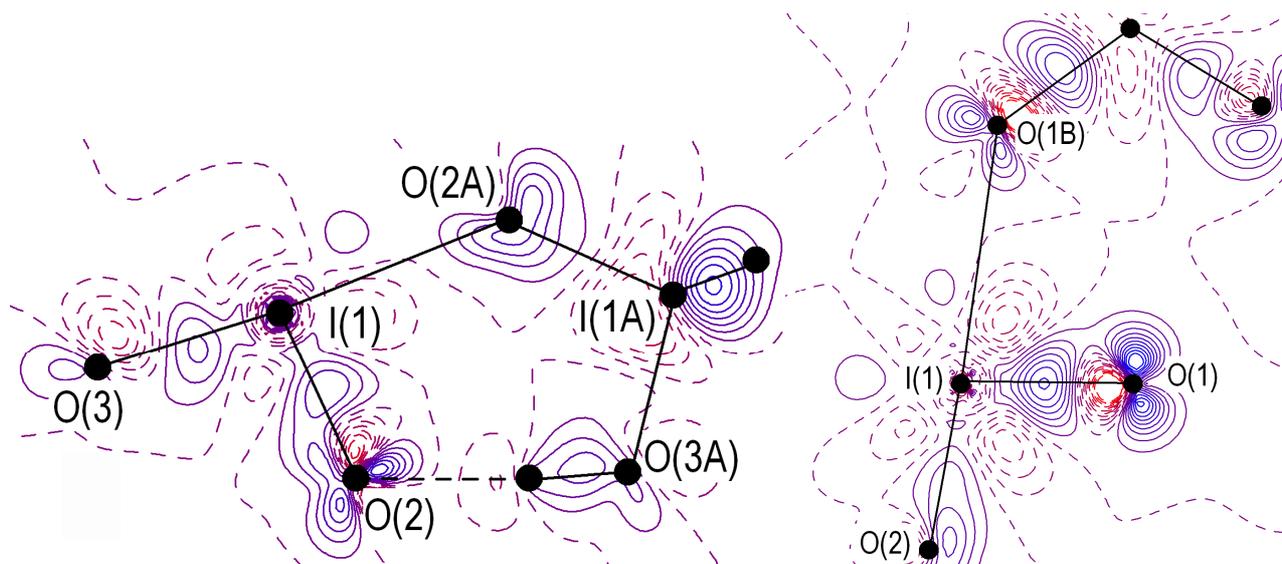
Figure S2 The sections of the DED distribution in the area of the I(1)−O(2A) and H-bonds and I…O(1B) interaction in α-HIO$_3$. The contours are drawn with the interval of 0.1 e$Å^{-3}$, the negative contours are dashed.

Table S1 Atomic charges according to the XRD data for α-HIO$_3$ and those obtained according to the DFT calculations, together with the atomic energies for the isolated dimer.

Atom	q, e (XRD)	q, e (DFT)[a]	$-E_{at}$, a.u. (DFT)[a]
I(1)	+2.20	+2.15 [+2.10]	6923.28386 [6923.31492]
O(1)	−0.95	−0.82 [−0.81]	75.22970 [75.22388]
O(2)	−0.85	−0.94 [−0.91]	75.27308 [75.25387]
O(3)	−0.83	−0.97 [−0.97]	75.34572 [75.36879]
H(3O)	+0.43	+0.56 [+0.61]	0.38568 [0.34558]

[a] The values for the second A-labeled molecule of HIO$_3$ are given in brackets.

Crystallographic data: Crystals of α-HIO$_3$ (M = 175.91) are orthorhombic, space group P2$_1$2$_1$2$_1$, at 100K: a = 5.49970(10), b = 5.84600(10) and c = 7.67120(11) Å, V = 246.639(7) Å^3, Z = 4 (Z' = 1), d_{calc} = 4.737 gcm^{-3}, μ(MoKα) = 126.96 cm^{-1}, F(000) = 312. Intensities of 3741 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, 2θ<120°] and 3741 independent reflections (R_{int} = 0.0160) were used in further refinement. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atom was located from the Fourier synthesis of the electron density and

refined in the isotropic approximation. The refinement converged to $wR_2 = 0.0369$ and GOF = 1.003 for all independent reflections [$R_1 = 0.0155$ was calculated against F for 3724 observed reflections with $I>2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

The multipole refinement was carried out using the XD program package.[1] Before the refinement, the O−H bond distance was normalised to the value of 1.00 Å obtained from the neutron diffraction data[2] and quantum chemical calculations (see below). The level of multipole expansion was octupole for oxygen atoms and hexadecapole for the iodine atom. The D_{10} term was refined for the hydrogen atom. The refinement was carried out against F. For **1** it converged to $R = 0.0110$, $Rw = 0.0141$ and GOF = 1.781 for 1198 merged reflections (including Friedel pairs) with $I>3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[3] (the largest difference of the mean square displacement amplitude along a bond was $10\cdot10^{-4}$ Å^2). The potential energy density function v($\mathbf{r}$) was evaluated through the procedure proposed in refs. 4, 5. Accordingly, the kinetic energy density function g($\mathbf{r}$) is described as $(3/10)(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{5/3}+(1/72)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})+1/6\nabla^2\rho(\mathbf{r})$, what in conjunction with the local virial theorem $(2g(\mathbf{r})+v(\mathbf{r})=1/4\nabla^2\rho(\mathbf{r}))$ leads to the expression for v($\mathbf{r}$) and makes possible to estimate the electron energy density $h_e(\mathbf{r})$. The total electron density function for HIO_3 was positive everywhere; the maximum (0.38 eÅ^{-3}) and minimum (–0.42 eÅ^{-3}) of residual electron density were located in the vicinity of the I(1) nucleus. Analysis of topology of the $\rho(\mathbf{r})$ function was carried out using the WinXPRO program package.[6]

The DFT calculations of the isolated molecule of HIO_3 and the H-bonded dimer were performed with the Gaussian09 program package[7] using the dispersion-corrected B97D functional.[8] Full optimization of their geometry was carried starting from the X-ray structural data with the Sadlej's standard polarised POL basis set[9] for the iodine atom and 6-311G+(d,p) one for all other atoms. The extremely tight threshold limits of $2\cdot10^{-6}$ and $6\cdot10^{-6}$ a.u. were applied for the maximum force and displacement, respectively. The optimization was followed by the evaluation of the harmonic vibration frequencies, revealing that the geometry obtained correspond to the stationary point. The topological analysis of the computed electron densities was performed using the AIMall program package.[10]

1. A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. Mallinson, T. Richter and T. Koritsanszky, *XD2006 - A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors*, 2006.
2. K. Stahl and M. Szafranski, *Acta Chem. Scand.*, 1992, **46**, 1146-1148.
3. F. L. Hirshfeld, *Acta Crystallogr. A*, 1976, **32**, 239-244.
4. Y. A. Abramov, *Acta Crystallogr. A*, 1997, **53**, 264-272.

5.   V. Tsirelson and A. Stash, *Acta Crystallogr. A*, 2004, **60**, 418-426.

6.   A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371-373.

7.   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz and J. Cioslowski, 2009.

8.   S. Grimme, *J. Comp. Chem.*, 2006, **27**, 1787-1799.

9.   A. J. Sadlej, *Collec. Czech. Chem. Commun.*, 1988, **53**, 1995.

10.   T. A. Keith, AIMAll (Version 10.12.13), 2010, http://aim.tkgristmill.com.

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