

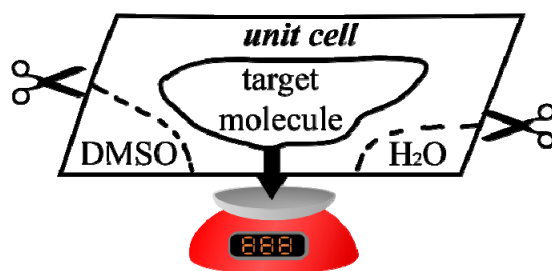
Density estimation method for individual compounds from X-ray diffraction analysis of their solvated forms

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SUPPLEMENTARY INFORMATION



X-ray experiment

Single crystals of **1** suitable for the X-ray study were obtained in the form of hydrate (1:1) by slow evaporation of the solution in water. At 100K, single crystals (C₅HN₇O₇·H₂O) are triclinic: $a = 6.2419(4)\text{\AA}$, $b = 6.4883(4)\text{\AA}$, $c = 24.9035(15)\text{\AA}$, $\alpha = 92.2670(10)^\circ$, $\beta = 90.5600(10)^\circ$, $\gamma = 90.6740(10)^\circ$, $V = 1007.66(11)\text{\AA}^3$, $Z = 4$, space group $P-1$, $d_{\text{cryst}} = 1.906 \text{ g}\cdot\text{cm}^{-3}$. Intensities of

21296 reflections were measured with SMART APEX II CCD diffractometer ($\lambda(\text{Mo-}K\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scans, $2\theta < 58.5^\circ$), and further processed using SAINT и SADABS codes, incorporated into the APEX2 software.^[1] The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation. The 5443 independent reflections [$R_{\text{int}} = 0.0534$] were used in the refinement procedure that was converged to $wR_2 = 0.1285$ calculated on F^2_{hkl} ($GOF = 1.044$, $R_1 = 0.0541$ calculated on F_{hkl} using 4083 reflections with $I > 2\sigma(I)$). The refinement was carried out with the SHELXTL program.^[2]

The Δ_{OED} – based densification approach

According to the approach, it is assumed that upon crystal formation, molecules interact to each other by means of overlap of their electron densities. It means that volume of isolated molecule is larger than that of the molecule in a crystal. Similarly, density of an isolated molecule (d_{mol}) is lower than that in a crystal (d_{cryst}). The latter is the density of the crystal structure obtained from X-ray experiment. In the other words, upon crystal structure formation, molecule is densified. The value of d_{mol} can be estimated by analysis of the electron density of optimized isolated molecule in terms of the AIM theory. It is defined as a ratio of molecular mass per molecular volume (the latter is presented as the sum of atomic volumes)

$$d_{\text{mol}} = m_{\text{mol}}/V_{\text{mol}}; \quad m_{\text{mol}} = M_{\text{mol}}/N_A; \quad V_{\text{mol}} = \sum_i V_{\text{at}}^{(i)}$$

Here, M_{mol} and m_{mol} are molar and molecular masses, respectively, N_A is Avogadro number, V_{mol} and V_{at} are molecular and atomic volumes, respectively. It is convenient to present d_{mol} in g/cm^3 units. Evidently, the volume and density of any molecular fragment can be calculated in a similar way. For estimation of V_{mol} , isodensity surface of $0.0004 \text{ e}/a_0^3$ (a_0 – Bohr radius) was utilized for integration procedure. So estimated molecular volume comprises about 99.8% of all electrons (nearly whole molecule), and charge leakage does not exceed $0.002 \text{ e}/\text{\AA}^3$ that approximately

corresponds to numerical error of integration of calculated electron density. It is evident, that difference between crystal and molecular density can be served as a measure of how pronounced is the overlap of molecular electron densities upon crystal structure formation. Therefore, the Δ_{OED} criterion defined as $\Delta_{\text{OED}} = d_{\text{cryst}} - d_{\text{mol}}$ would characterize a degree of molecular densification and, therefore, tightness of crystal packing. Combined analysis of d_{mol} and Δ_{OED} values would clarify an origin of the observed crystal density.

In the case of one molecule in the asymmetric unit cell, density of a molecule in a crystal is simply equal to crystal density that is obtained from X-ray experiment. For estimation of density of an isolated molecule, its geometry was calculated at the M052X/6-311G(df,pd) level of theory that was successfully utilized in our recent studies on polynitro compounds. The GAUSSIAN program was used for calculation.^[3] The wave functions obtained from calculation of isolated molecules were analyzed in terms of R. Bader "AIM" topological theory^[4] using the AIMALL program.^[5]

However, the Δ_{OED} – based approach can be applied not only to the whole molecule, but also to any molecular unit or structural unit, if there are more than one structural unit in the asymmetric unit cell. In such case one needs to define a way of estimation of the volume of the unit in a crystal. To do this, one can generate cluster in which the unit under study is surrounded by its environment. The supramolecular clusters are generated in such a way that each atom of the unit has all geometric contacts within the sphere of 5 Å radii. To obtain electron density distribution in such clusters, lower level of theory, namely, HF/3-21G is used because of huge size of a cluster. AIM partitioning of so obtained electron density can be carried out using the MultiWFN program.^[6]

References

1. APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2013.
2. G. M. Sheldrick, *Acta Crystallogr.*, **2015**, *C71*, 3-8.
3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Kudin, K. N., Jr.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.;

- Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*, Gaussian, Inc.: Wallingford, 2004.
4. Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.
 5. Keith, T. A. **2014**, *AIMAll, Version 14.11.23*. TK Gristmill Software, Overland Park KS, USA (<http://aim.tkgristmill.com>)
 6. T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592.