Mendeleev Commun., 2003, 13(2), 60–62

Intramolecular H-bonds in the crystal of tetraacetylethane: 3c-4e interaction or a dynamic disorder?

Konstantin A. Lyssenko,* Denis V. Lyubetsky and Mikhail Yu. Antipin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru

10.1070/MC2003v013n02ABEH001696

The analysis of the experimental electron density function and anisotropic displacement parameters in tetraacetylethane has revealed that the intramolecular O–H···O bond corresponds to the intermediate type of interatomic interactions and that the variation of the C–O and C–C bond lengths with temperature (110–298 K) is the result of the dynamic disorder (superposition of tautomers) due to interatomic C–H···O contacts.

High-resolution X-ray diffraction analysis of systems with low-barrier strong O–H···O hydrogen bonds are of great interest for studying symmetrical H-bonding, *i.e.*, the 3-centre 4-electron (3c-4e) O–H–O interaction.[1,2] However, such investigations are often difficult to perform because of a static or dynamic disorder in the area of H-bond formation (either the presence of both tautomers or rapid proton transfer in a crystal).[1(*a*),3] Hence, for the interpretation of X-ray diffraction data, it is preferable to analyse crystal structures in a wide temperature interval. A special attention should be given to the analysis of anisotropic atomic displacement parameters, which allow one to reveal systematic errors caused by the superposition of tautomers.[1(*a*),3]

In particular such problems arise in the case of symmetrical systems, which are most interesting in terms of 3c-4e O–H···O bonding, *e.g.*, acetylacetone (acac).[3(*b*)] X-ray diffraction studies of acac at 110 K have revealed that the symmetry plane (space group *Pnma*, $Z = 4$) in a crystal passes through the midpoint of the O···O line perpendicular to the plane of the molecule. Hence, the correct elucidation of the O–H···O bond nature and the type of disorder in a crystal of acac is impossible.[3(*b*)]

However in the similar compound tetraacetylethane (tacet) the neutron diffraction analysis at 298 K[4] revealed that this molecule occupies a special position on the two fold axis with all atoms of one of the keto–enol rings in general positions (Figure 1). Taking into account the significant shortening of the O···O distance up to 2.450 Å in tacet (in acac, O···O is 2.547 Å), as well as the pronounced equalisation of C–O, C=O and C–C, C=C bond lengths in the keto–enol ring, it was interesting to analyse the H···O interaction in this symmetrical system.

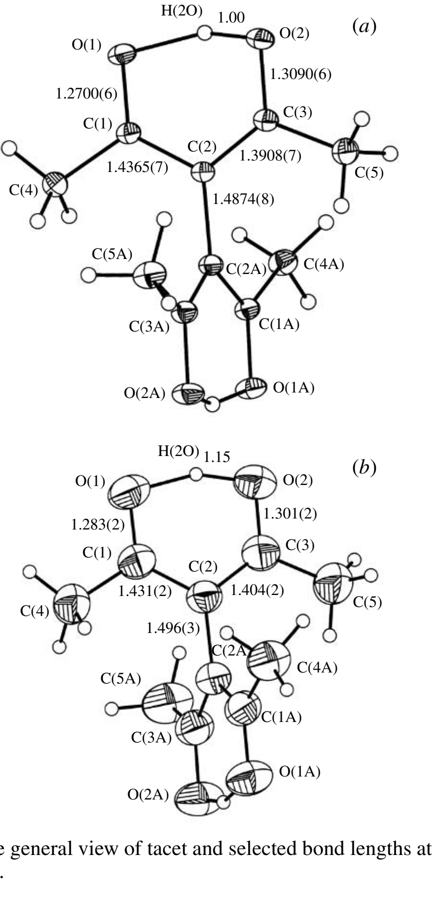

Figure 1 The general view of tacet and selected bond lengths at (*a*) 110 K and (*b*) 298 K.

An X-ray diffraction study of tacet at 110 K[†] has demonstrated that molecular geometry is significantly changed in comparison to neutron diffraction data at 298 K[4] (Figure 1). Thus, upon crystal cooling, the delocalization of π-density in the six-

---

[†] *Crystallographic data for* tacet: crystals of $C_{10}H_{14}O_4$ ($M = 238.27$) are orthorhombic, space group *Pbcn*, at 110 K: $a = 9.078(1)$, $b = 9.251(1)$, $c = 11.526(1)$ Å, $V = 968.0(2)$ Å^3, $Z = 4$, $d_{calc} = 1.360$ g cm^{-3}, μ(MoKα) = = 1.05 cm^{-1}, $F(000) = 424$; at 298 K $a = 9.139(1)$, $b = 9.392(1)$, $c = 11.853(2)$ Å, $V = 1017.3(2)$ Å^3, $Z = 4$, $d_{calc} = 1.294$ g cm^{-3}, μ(MoKα) = 1.00 cm^{-1}, $F(000) = 424$. Intensities of 23771 (110 K) and 6872 (298 K) reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω 10–20 s per frame exposure, $2\theta < 100°$ (110 K) and 58° (298 K)]; 4904 (110 K) and 1330 (298 K) independent reflections [$R_{int} = 0.0269$ (110 K) and 0.0254 (298 K)] were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1071$ and GOF = 1.025 for all independent reflections [$R_1 = 0.0493$ was calculated against F for 3806 observed reflections with $I > 2\sigma(I)$] at 110 K and to $wR_2 = 0.1045$ and GOF = 0.977 for all independent reflections [$R_1 = 0.0518$ was calculated against F for 965 observed reflections with $I > 2\sigma(I)$] at 298 K. All calculations were performed using the SHELXTL PLUS 5.0 on IBM PC AT.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 208548 and 208549. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

The analytical form of the electron density was obtained by a multipole refinement based on the Hansen–Coppens[10] formalism using the XD program[11] package. All C-H bond distances were normalised to the ideal value 1.08 Å. The O(2)–H(2O) distance was obtained through the B3LYP/6-31G** calculation using the G98W program package. The geometry in an isolated state was in a good agreement with the experimental [*e.g.*, the O···O distance was 2.464 and 2.437(1) Å, and the O(2)–H(2O) and H(2O)···O(1) distances were equal to 1.015 and 1.460Å, respectively]. The level of the multipole expansion was octopole for all non-hydrogen atoms and dipole for hydrogens. The H(2O) atom that forms the intermolecular H-bond was refined up to quadropole level. The scattering factor of the hydrogen atoms was calculated from the contracted radial density functions ($k = 1.2$). The refinement was carried out against F, the multipole occupancies of the oxygen and carbon atoms of the keto–enol cycle were refined with the m symmetry restraints according to ref. 12. The refinement converged to $R = 0.0360$, $wR = 0.0350$, GOF = 0.88 for 2716 reflections with $I > 3\sigma(I)$. The subsequent analysis of the deformation electron density, the topology of the $\rho(r)$ function and ELF[15(*b*)] was carried out using the WINXPRO 1.1 program package.[13]

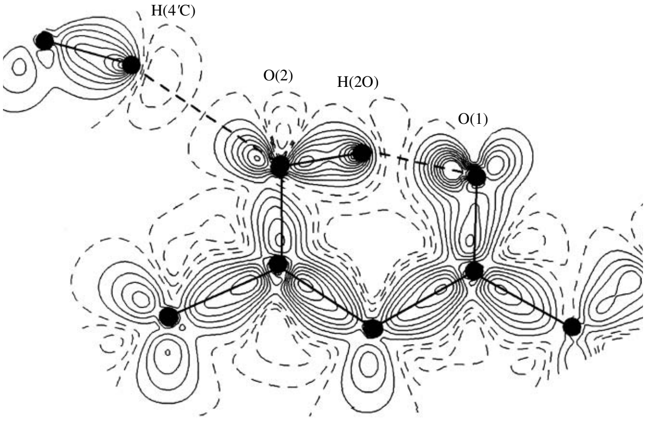

Figure 2 The DED distributions in the plane of the keto–enol ring of tacet. Contours are drawn with a 0.1 eÅ^{-3} interval. The negative contours of DED are dashed.

membered H-bonded ring, which can be estimated by the degree of equalisation of bond lengths, is reduced, and the *Q* value[5] (sum of the differences of C=O, C–O and C=C, C–C bond lengths) changes from 0.033 to 0.085 Å at 110 and 298 K, respectively.

In order to compare experimental data at different temperatures for the same single crystal of tacet, an X-ray diffraction study was also carried out at 298 K.[†] The obtained geometry is close to neutron diffraction data, in particular, the Q value calculated with the account of libration correction, was equal to 0.045 Å.

To reveal possible disorder in the tacet, we analysed anisotropic atomic displacement parameters within the LTS rigid-body model (calculations were performed using the THMA-11 program[6]). The tacet molecule in the crystal at both temperatures is structurally rigid (the R_u value varied from 6.2 to 7.6%). The analysis of the mean-square displacement amplitudes (Δ)[7] demonstrated that, at 110 K, all bonds satisfy Hirshfeld rigid-bond criteria (the average value of Δ is 6.6×10^{-4} Å^2), whereas the corresponding Δ values exceed 28×10^{-4} Å^2 at 298 K.

Thus, the observed equalisation of the C–C and C–O bond lengths in the crystal of tacet at 298 K and the shortening of the O(1)···H(2O) bond (Figure 1) result from a dynamic disorder caused by the superposition of tautomers rather than electron density delocalization and the formation of an intramolecular 3c-4e H-bond.

Taking into consideration the dynamic nature of the disorder in the crystal of tacet, we assumed that the non-equivalence of tautomers may result from shortened intermolecular interactions, the strength of which decreases with temperature. Indeed, the analysis of the crystal packing revealed that the O(2) atom participated in the intermolecular C–H···O contact of a moderate strength [O(2)···H(4′C)–C(4′) (–1/2 + *x*, –1/2 + *y*, 1/2 – *z*), O(2)···H(4′C) 2.32 Å, O(2)···C(4′) 3.368(1) Å, O(2)–H(4′C)–C(4′) 163°]. Note that the C···O distance, characterising the strength of this contact, increases from 3.369(1) to 3.407(2) Å at 110 and 298 K, respectively. Thus, the shortening of this contact upon crystal cooling rises proton transfer barrier leading to the crystal structure ordering at 110 K.

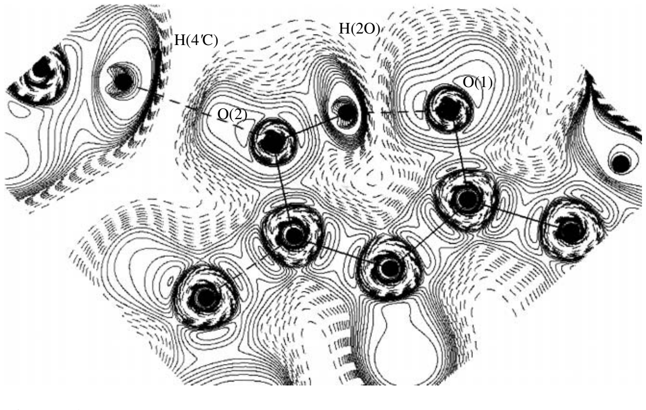

Figure 3 The ELF distribution in the plane of the keto–enol ring of tacet; contours are drawn at 0.1 intervals. The values of ELF < 0.5 are dashed.

To investigate the H-bonding and the role of crystal packing in a proton transfer barrier, we performed a topological analysis of electron density distribution in terms of the ‘Atoms in Molecules’ (AIM)[8] theory and an electron localization function (ELF)[9] on a basis of X-ray diffraction data at 110 K.

The analysis of critical points (CP) (3, –1) revealed that the intramolecular O–H···O and intermolecular C–H···O contacts correspond to a chemical bond within the framework of the AIM theory.[9] Topological parameters of the $\rho(r)$ function in the CP (3, –1) of C–O and C–C bonds in the keto–enol cycle correspond to the shared type of interatomic interactions [the values of $\nabla^2\rho(r)$ are negative] and are close to the corresponding values in 3-acetyl-4-hydroxycoumarine.[1(*b*)] In contrast, while the values of $\nabla^2\rho(r)$ in the CP (3, –1) of C–H···O and O–H···O contacts are both positive (1.09 and 8.44 eÅ^{-5}), the type of these interactions is different.

The analysis of the deformation electron density (DED) distribution demonstrated a pronounced polarisation of electron density accumulation corresponding to electron lone pairs (Lp) of oxygen atoms and its local depletion in the O···H region of both contacts (Figure 2). Thus, the DED distribution in the O–H···O area in tacet is in agreement with the corresponding distribution for similar keto–enol systems with asymmetrical H-bonds.[1(*b*),(*e*)]

In contrast to the DED map, the distinctions of ELF distribution for these interactions are more pronounced. In the region of the intramolecular O–H···O bond, the continuous ELF distribution with the polarisation of O(1) atom Lp and the deformation of the H(2O) atom valence shell [the decrease of ELF in the H(2O)···O(1) direction] were found (Figure 3). Note that a similar distribution was recently found for the strong intermolecular O–H···O bond in the crystal of diphenylphosphonic acid.[14] At the same time, despite a similar polarisation of the O(2) atom Lp and a deformation of the H(4′C) valence shell, the C–H···O contact is characterised by a discontinuous ELF distribution.

The peculiarities of the ELF distribution in the area of the intra- and intermolecular H-bonds in tacet[15] are general features of shared and closed shell interatomic interactions, respectively. Indeed, the local electron energy densities [$E(r)$] in CP(3, –1) of the O(1)···H(2O) and H(4′C)···O(2) contacts, estimated on the basis of a semi-quantitative description of kinetic energy density,[16] are equal to –0.016 and 0.032 a.u., respectively. Taking into account that the above values of $\nabla^2\rho(r)$ for these contacts are positive, the estimated $E(r)$ values unambiguously indicate that the O–H···O bond corresponds to an intermediate type of interatomic rather than shared (*i.e.*, covalent) interactions. Topological characteristics of the C–H···O contact are common for weak interactions of a closed-shell type.[8] The intermediate type of the O–H···O interaction is also in agreement with the high value of $\rho(r)$ (0.56 eÅ^{-3}) in the CP (3, –1) in comparison with that (0.04 eÅ^{-3}) for the C–H···O contact.

In spite of an insignificant value of $\rho(r)$ in the CP (3, –1) of the C–H···O contact in tacet, the energy of this interaction, estimated from the potential energy density,[17] is equal to ~1.5 kcal mol^{-1}. Therefore, the intermolecular interaction can lead to the inequivalence of keto–enol tautomers in the crystal and affect the barrier of proton transfer.

Thus, the equalisation of bond lengths at 298 K in tacet is due to the superposition of tautomers (dynamic disorder) and the ordering of the crystal structure at 110 K resulted from the rise of the barrier proton transfer because of one intermolecular C–H···O contact.

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32214).

References

1 (*a*) G. Gilli and P. Gilli, *J. Mol. Struct. (Theochem)*, 2000, **552**, 1; (*b*) K. A. Lyssenko and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 400 (*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 418); (*c*) G. K. H. Madsen, B. B. Iversen, F. K. Larsen, M. Kapon, G. M. Reiser, F. H. Herbstein, *J. Am. Chem. Soc.*, 1998, **120**, 10040; (*d*) B. Schiott, B. B. Iversen, G. K. H. Madsen and T. C. Bruice, *J. Am. Chem. Soc.*, 1998, **120**, 12117; (*e*) P. Roversi, M. Barzaghi, F. Merati and R. Destro, *Can. J. Chem.*, 1996, **74**, 1145; (*f*) P. Macchi, B. B. Iversen, A. Sironi, B. C. Chaukoumakos and F. K. Larsen, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 2719.

2 (*a*) V. G. Tsirelson and R. P. Ozerov, *Electron Density and Bonding in Crystals: Principles, Theory and X-Ray Diffraction Experiments in Solid State Physics and Chemistry*, IOP Publishing Ltd, Bristol, 1996; (*b*) T. S. Koritsanszky and P. Coppens, *Chem. Rev.*, 2001, **101**, 1583.

3 (*a*) F. H. Herbstein, B. B. Iversen, M. Kapon, F. K. Larsen, G. K. H. Madsen and G. M. Reisner, *Acta Crystallogr.*, 1999, **B55**, 767; (*b*) R. Boese, M. Yu. Antipin, D. Blaeser and K. A. Lyssenko, *J. Phys. Chem.*, 1998, **B102**, 8654.

4 L. F. Power, K. E. Turner and F. H. Moore, *J. Cryst. Mol. Struct.*, 1975, **5**, 59.

5 (*a*) G. Gilli, F. Bellucci, V. Ferretti and V. Bertolasi, *J. Am. Chem. Soc.*, 1989, **111**, 1023; (*b*) V. Bertolasi, P. Gilli, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1991, **113**, 4917; (*c*) P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1994, **116**, 909; (*d*) G. Gilli, V. Bertolasi, V. Ferretti and P. Gilli, *Acta Crystallogr.*, 1993, **B49**, 564.

6 T. Maverick and K. N. Trueblood, *Thermal Motion Analysis Program THMA-11*, Zurich, 1987.

7 F. L. Hirshfeld, *Acta Crystallogr.*, 1976, **A32**, 239.

8 (*a*) R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990; (*b*) R. F. W. Bader, *J. Chem. Phys.*, 1998, **A102**, 7314; (*c*) R. F. W. Bader and H. Essen, *J. Chem. Phys.*, 1984, **80**, 1943; (*d*) R. F. W. Bader, S. Johnson, T. H. Tang and P. L. A. Popelier, *J. Phys. Chem.*, 1996, **100**, 15398.

9 A. Savin, R. Nesper, S. Wengert and T. Fassler, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1808.

10 N. K. Hansen and P. Coppens, *Acta Crystallogr.*, 1978, **A34**, 909.

11 T. Koritsansky, S. T. Howar, T. Richter, P. R. Mallinson, Z. Su and N. K. Hansen, *XD, a Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-ray Diffraction Data*, 1995.

12 K. Kurki-Suonio, *Israel J. Chem.*, 1977, **16**, 115.

13 (*a*) A. Stash and V. Tsirelson, *WinXPRO – a Program for Calculation of the Crystal and Molecular Properties Using The Model Electron Density*, 2001. A further information available at *http://xray.nifhi.ru/wxp/*; (*b*) A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371.

14 K. A. Lyssenko, G. V. Grintchelev-Knyazev and M. Yu. Antipin, *Mendeleev Commun.*, 2002, 128.

15 (*a*) F. Fuster and B. Silvi, *Teor. Chem. Acc.*, 2000, **104**, 13; (*b*) V. Tsirelson and A. Stash, *Chem. Phys. Lett.*, 2002, **351**, 142.

16 D. A. Kirzhnits, *Sov. Phys. JETP*, 1957, **5**, 64.

17 E. Espinosa, E. Mollins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.

Received: 6th December 2002; Com. 02/2022