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On H···H distances and the van der Waals radius of hydrogen in inorganic and organic compounds.

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Abstract

The short H···H contacts of the head-to-side type of about 2.05 Å described recently as having been found in carbohydrates [Steiner & Saenger (1991). *Acta Cryst.* **B47**, 1022–1023] complement nicely the observations on inorganic hydroxides and hydrates, which led to a revision of the van der Waals radius of hydrogen to 1.0 Å [Baur (1972). *Acta Cryst.* **B28**, 1456–1465]. For the case of side-to-side contacts a different behaviour is diagnosed for organic and inorganic crystal structures: side-on contacts in inorganic compounds can be shorter than the head-on contacts are, while in organic compounds the opposite is true.

Introduction

Steiner & Saenger (1991) have recently reported on H···H van der Waals distances in cooperative O—H···O—H···O hydrogen bonds as found in 23 crystal structures of carbohydrates determined by neutron diffraction methods. The minimal value of the H···H distance, $d_{\mathrm{HH,min}}$, is found by these authors to be about 2.05 Å for the case of head-to-side contacts (a head-on contact is in the direction of the O—H vector, a side-on contact is at an angle of about 90° from the head-on contact). This is considerably less than the 2.4 Å that the sum of two van der Waals radii of the H atom current about 30 years ago would indicate (r_{H} = 1.2 Å, Pauling, 1960). The authors were aware of individual reports of short H···H contacts, but not of any systematic analysis of such distances. Actually there is at least one such report in the literature (Baur, 1972), which is nicely complemented by the new study of Steiner & Saenger (1991).

Discussion

On the basis of an inspection of 60 inorganic crystal structures containing OH groups and water molecules and determined by neutron diffraction methods it was shown (Baur, 1972):

(1) The shortest H···H distances occur in water molecules, $d_{\mathrm{HH,min}}$ about 1.5 Å, when two H atoms are covalently bonded to one oxygen atom.

(2) Under special circumstances, such as the tight packing of parallel, but oppositely oriented, OH groups in brucite, $Mg(OH)_2$, H atoms can come as close as 1.93 Å (Zigan & Rothbauer, 1967) to each other; there is no hydrogen bonding involved in this case.

(3) In cases where the same electronegative atom is acting as both the donor and the acceptor atom in different hydrogen bonds, $d_{\mathrm{HH,min}}$ between the donated and the accepted H atoms can be as short as 2.05 Å; this last case corresponds exactly to the situation described by Steiner & Saenger (1991) for the carbohydrates studied by them.

From this it was concluded that the then current van der Waals radius of hydrogen (1.2 Å) was unnecessarily large. A value of 1.0 Å was proposed for the van der Waals radius of hydrogen (Baur, 1972), without distinguishing between head-on and side-on radii. The observations on the carbohydrates fit very well with that revised value of the radius of the H atom. It seemed in 1972 that the same criteria applying to hydrogen bonds in inorganic compounds should also apply to hydrogen bonds in organic compounds. This has now been verified for the case of head-to-side radii in carbohydrates by the work of Steiner & Saenger (1991), see (3) above.

Nyburg, Faerman & Prasad (1987) found the side-on radii of hydrogen bonded to carbon to be 0.25–0.38 Å longer than the corresponding head-on radii (in the absence of hydrogen bonds). The authors called this the polar flattening of the H atom.

This latter observation does not find its counterpart among inorganic structures. Case (2) above refers to a side-to-side contact (or side-on contact) of H atoms in the crystal structure of brucite, $Mg(OH)_2$, which crystallizes in the CdI_2 structure type. In this case each H atom has three H-atom neighbors at a distance of 1.93 Å. An even shorter H—H distance of 1.83 Å has been reported in the isostructural compound $Ni(OH)_2$ (Szytula, Murasik & Balanda, 1971). Longer H—H distances are known from the isostructural hydroxides $Mn(OH)_2$, 1.99 Å (Christensen & Ollivier, 1972), and $Ca(OH)_2$, 2.19 Å (Busing & Levy, 1957). In these four crystal structures the H—H distances are simply a function of the ionic radius of the cation. The coordination octahedra in the CdI_2 structure type share edges with each other. The smaller the octahedron, the more the H atoms (which are not involved in hydrogen bonding) are pressed together. Apparently the side-on radius of hydrogen in this type of compound is shorter and may be softer than the head-on radius. In any event the H atom in these surroundings must be described as prolate, with a side-on radius of about 0.9 Å, that is shorter than in the head-on direction (and exactly opposite to the oblate shape of the H atoms in organic compounds). The different radii of H atoms in different directions in organic and inorganic crystal structures might be due to the difference between molecular compounds on the one hand, where it would be difficult to realize conformations in which the H atoms would be pressed together, and on the other hand frameworks where an imposed internal compressive force cannot be avoided by the H atoms.

References

Baur, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.

0108-7681/92/050745-02$06.00

CHRISTENSEN, A. N. & OLLIVIER, G. (1972). *Solid State Commun.* **10**, 609–614.
NYBURG, S. C., FAERMAN, C. H. & PRASAD, L. (1987). *Acta Cryst.* **B43**, 106–110.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
STEINER, T. & SAENGER, W. (1991). *Acta Cryst.* **B47**, 1022–1023.
SZYTULA, A., MURASIK, A. & BALANDA, M. (1971). *Phys. Status Solidi B*, **43**, 125–128.
ZIGAN, F. & ROTHBAUER, R. (1967). *Neues Jahrb. Mineral. Monatsh.* pp. 137–143.

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X-ray powder diffraction studies of *n*-alkanes: a re-examination of the unit-cell parameters of $C_{24}H_{50}$ and $C_{26}H_{54}$.

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Abstract

Further analysis of the synchrotron X-ray powder diffraction patterns for *n*-tetracosane ($C_{24}H_{50}$) and *n*-hexacosane ($C_{26}H_{54}$) has yielded unit cells in addition to those proposed by Gerson, Roberts & Sherwood [*Acta Cryst.* (1991), **B47**, 280–284]. The new unit cells are very similar to those predicted by Nyburg & Potworowski [*Acta Cryst.* (1973), **B29**, 347–352] being triclinic and conforming to the series observed for $C_{18}H_{38}$, $C_{20}H_{42}$ and $C_{22}H_{46}$ [Gerson, Roberts & Sherwood (1991). *Acta Cryst.* **B47**, 280–284].

Discussion

Ab intio indexing (using the program *ITO*, Visser, 1969) of the synchrotron radiation powder diffraction patterns of $C_{24}H_{50}$ and $C_{26}H_{54}$ seemed to indicate bilayer $Z = 2$ pseudomonoclinic unit cells (Gerson, Roberts & Sherwood, 1991). From these unit cells a polytypic form of the triclinic $Z = 1$ type structure ($C_{18}H_{38}$, Nyburg & Lüth, 1972), was proposed. These unit cells did not agree with those predicted by Nyburg & Potworowski (1973). A single-crystal X-ray diffraction study (Gerson & Nyburg, 1992) has since shown $C_{24}H_{50}$ to be isostructural to the shorter even *n*-alkanes ($C_{20}H_{42}$, Nyburg & Gerson, 1992; $C_{18}H_{38}$, Nyburg & Lüth, 1972) as predicted. This result led us to re-examine our previous analysis of the powder data recorded for $C_{24}H_{50}$ and for $C_{26}H_{54}$.

The unit cells predicted by Nyburg & Potworowski (1973) for $C_{24}H_{50}$ and $C_{26}H_{54}$ were refined, using the program *ITO* (Visser, 1969), against the reflection positions observed (Gerson, Roberts & Sherwood, 1991). The resulting unit cells were then further refined against the indexed reflections using *REFCEL* (Daresbury Laboratory Powder Diffraction Library).

The newly refined $Z = 1$ unit cells (Table 1) were found to predict the reflection positions at least as well as the polytypic unit cells previously proposed (Gerson, Roberts & Sherwood, 1991). The proposed $Z = 2$ pseudomonoclinic unit cells for $C_{24}H_{50}$ and $C_{26}H_{54}$ are most probably the result of incorrect indexing. Both compounds almost certainly have the same triclinic $Z = 1$ lattice as observed for the shorter even *n*-alkanes ($C_{18}H_{38}$ to $C_{22}H_{46}$, Gerson, Roberts & Sherwood, 1991).

Table 1. *Measured and predicted* (*Nyburg & Potworowski*, 1973) *unit cells of* $C_{24}H_{50}$ *and* $C_{26}H_{54}$ *with e.s.d.'s below in parentheses*

(*a*) Figure of merit.* (*b*) Number of peak positions used as data in *ITO*.

	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å³)	*Z*	(*a*)	(*b*)
$C_{24}H_{50}$	4.277	4.817	32.544	86.29	68.86	72.74	597	1	47	40
	(0.001	0.001	0.005	0.02	0.03	0.03)				
$C_{24}H_{50}$†	4.285	4.82	32.50	86.43	68.71	72.70	596	1		
$C_{26}H_{54}$	4.269	4.803	34.883	86.92	69.94	73.10	642	1	45	40
	(0.001	0.001	0.005	0.05	0.05	0.03)				
$C_{26}H_{54}$†	4.285	4.82	35.04	86.73	68.92	72.70	644	1		

* See Gerson, Roberts & Sherwood (1991).
† Predicted.

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References

GERSON, A. R. & NYBURG, S. C. (1992). *Acta Cryst.* **B48**. 737–741.
GERSON, A. R., ROBERTS, K. J. & SHERWOOD, J. N. (1991). *Acta Cryst.* **B47**, 280–284.
NYBURG, S. C. & GERSON, A. R. (1992). *Acta Cryst.* **B48**, 103–106.
NYBURG, S. C. & LÜTH, H. (1972). *Acta Cryst.* **B28**, 2992–2995.
NYBURG, S. C. & POTWOROWSKI, J. A. (1973). *Acta Cryst.* **B29**, 347–352.
VISSER, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.

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