nearly 90° to each other. Substances like SF_6 and CBr_4 have plastic phases in which the molecules re-orient between equivalent directions. The butane molecule has no such symmetry equivalents, neither does the disorder introduce a higher mean structural symmetry.

It is interesting however to note the similarities between the structures of *n*-butane and 1,2-dichloroethane since the molecules of both are of a similar shape. The unit cell, space group and packing of butane in phase II are very close to those of dichloroethane in its only low-temperature state, and the orientationally disordered phases are similarly alike (Reed & Lipscomb, 1953; Milberg & Lipscomb, 1951). Butane, however, has an additional stable phase III. It is the transition from phase III to phase I which causes butane to have a discontinuity in its specific heat and hence a true phase transition, whereas dichloroethane does not.

We end by reminding the reader of the unexplained broadening of some peaks in phase II. Although several hypotheses can be propounded, the possibility of analysing for a peak-shape broadening function has been lost by the instrumental broadening. However, when very high resolution becomes available through back scattering from a spallation or synchroton source, a new field of science may be opened up, exploiting the detail that we are beginning to see in this work.

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References

Aston, J. G. & Messerly, G. H. (1940). *J. Am. Chem. Soc.* **62**, 1917-1923.

Bonham, R. A. & Bartell, L. S. (1959). *J. Am. Chem. Soc.* **81**, 3491-3496.

Cangeloni, M. L. & Schettino, V. (1975). *Mol. Cryst. Liq. Cryst.* **31**, 219-231.

Dolling, G., Powell, B. M. & Sears, V. F. (1979). *Mol. Phys.* **37**, 1859-1883.

Ewen, B. & Strobl, B. R. (1980). *Faraday Discuss. Chem. Soc.* **69**, 19-31.

Goldstein, H. (1959). *Classical Mechanics*, p. 143ff. Reading, MA: Addison-Wesley.

Hewat, A. W. & Bailey, I. (1976). *Nucl. Instrum. Methods*, **137**, 463-471.

Hoch, M. J. R. (1976). *J. Chem. Phys.* **65**(1), 2522-2526.

Howard, C. J. (1982). *J. Appl. Cryst.* **15**, 615-620.

Kohlbeck, F. & Hoerl, E. M. (1978). *J. Appl. Cryst.* **11**, 60-61.

Kuchitsu, K. (1961). *Bull. Chem. Soc. Jpn*, **32**, 748-769.

Millberg, M. E. & Lipscomb, W. N. (1951). *Acta Cryst.* **4**, 369-373.

Pawley, G. S. (1980). *J. Appl. Cryst.* **13**, 630-633.

Pawley, G. S. (1981). *J. Appl. Cryst.* **14**, 357-361.

Pitzer, K. S. (1940). *J. Am. Chem. Soc.* **62**, 331-335.

Reed, T. B. & Lipscomb, W. N. (1953). *Acta Cryst.* **6**, 45-48.

Ungar, G. (1983). *J. Phys. Chem.* **87**, 689-695.

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The Correlation Between Hydrogen-Bond Lengths and Proton Chemical Shifts in Crystals

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Abstract

A critical evaluation of the neutron diffraction crystal structure data used in correlating proton chemical-shift tensors with hydrogen-bond distances indicates that there is a linear relationship between the H···O bond length and the trace of the anisotropic chemical shift that extends from the short bonds observed with hydrogen-bonded anions to the long bonds from the water molecules in hydrated salts and carboxylic acids.

Introduction

Recent advances in solid-state NMR spectroscopy (Mehring, 1983; Fyfe, 1983) have prompted a dialogue between the crystallographers and the NMR spectroscopists. Some interesting correlations have been made between the results of crystal structure analyses and the traces of the ^{13}C anisotropic chemical-shift tensors obtained by the CP/MAS (cross-polarization magic-angle spinning) method for powdered specimens (Jeffrey, Wood, Pfeffer & Hicks,

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1983; Taylor, Marchessault, Perez, Stephenson & Fyfe, 1985). More interesting from the crystallographer's point of view are the measurements of the complete anisotropic chemical-shift tensors using single crystals, since this can be the new NMR crystallography. This field has been further stimulated by progress in calculating proton chemical-shift tensors for simple model systems using *ab initio* quantum mechanics (Ditchfield, 1976; Rohlfing, Allen & Ditchfield, 1983).

We noted that in two recent studies of the correlations between proton anisotropic chemical shifts and the hydrogen-bonding geometry in crystals (Rohlfing, Allen & Ditchfield, 1983; Berglund & Vaughan, 1980), only the O···O separations were considered. The O···O separation of a hydrogen bond is a function of three quantities, the O–H covalent bond length, the H···O hydrogen-bond length, and the O–H···O angle, which is seldom 180° in crystals. The practice of referring to the O···O separation as a hydrogen-bond length still persists, although it became obsolete about twenty years ago when the introduction of single-crystal diffractometers made it possible to locate hydrogen atoms by X-ray crystal structure analysis.

Of the twenty-five crystal structure analyses referenced in the aforementioned studies (Rohlfing, Allen & Ditchfield, 1983; Berglund & Vaughan, 1980), fifteen were, in fact, neutron diffraction analyses capable of providing hydrogen atomic positions nearly as precisely as those of the non-hydrogen atoms. For the remaining X-ray analyses, more reliable H···O hydrogen-bond distances could be obtained by normalizing the covalent O–H to a standard neutron diffraction value of 0·97 Å (Taylor & Kennard, 1983), if the hydrogen-atom coordinates were reported. Since these additional crystallographic data, which relate more directly to the structural environment of the hydrogen-bonding proton, were not utilized in the original work (Rohlfing, Allen & Ditchfield, 1983; Berglund & Vaughan, 1980), we are presenting them in this paper.

The data

Table 1 shows the relevant data for the same crystal structures as referenced in the previous publications (Rohlfing, Allen & Ditchfield, 1983; Berglund & Vaughan, 1980), with one exception. We have used a later neutron analysis of KH_2PO_4 (Kennedy, Nelmes, Thornley & Rouse, 1976). All the H···O distances and O–H···O angles were recalculated from the atomic coordinates and unit-cell dimensions reported in the original papers. The values of the trace of the proton anisotropic shift tensor, $\bar{\sigma}$, and of the anisotropy of the tensor $\Delta\sigma$, were obtained from the original papers referenced previously (Rohlfing, Allen & Ditchfield, 1983; Berglund & Vaughan, 1980).

The hydrogen bonds have been ordered into the three categories of molecular structure: the anions that form short strong bonds, the carboxylic acids, and the hydrates where weak longer bonds are formed by the water molecules. In each category, the bonds are arranged in sequence of increasing length. The data for malonic acid and potassium hydrogen maleate, which were included in the previous publication (Berglund & Vaughan, 1980), had to be omitted because no hydrogen coordinates were reported in these early X-ray studies.

The following points are noted concerning the neutron diffraction crystallographic data:

(1) The data points from potassium hydrogen malonate, 1, and ammonium dihydrogen phosphate, 2, refer to crystallographically symmetrical O···H···O hydrogen bonds. These room-temperature experiments cannot distinguish between symmetrical and static disordered unsymmetrical bonds. An actual hydrogen-bond distance up to 1·30 Å cannot be excluded.

(2) The two data from $KH_3(SeO_3)$, 6 and 6′, would be consistent with the other data if the bond lengths *vs* $\bar{\sigma}$ and $\Delta\sigma$ assignments were reversed.

(3) Of the carboxylic acid data, 11 to 15, only that of trichloroacetic acid, 14, has the closed-dimer hydrogen bonding, which was the model used for the theoretical calculations (Rohlfing, Allen & Ditchfield, 1983).

(4) In α-selenous acid, 17 and 17′, it is relevant to note that the two OH stretching frequencies show an anomalously large splitting, 2300 and 2900 cm^{-1}, which is interpreted as due to 'a strong coupling of the two OH groups through the selenium atom' (Falk & Giguere, 1958).

(5) The $MgSO_4.H_2O$ datum, 18, is from a neutron powder diffraction analysis which may be less definitive than a single-crystal analysis.

(6) The $CaSO_4.2H_2O$ datum, 19, is a refinement based on very old (1958) neutron data.

(7) In α-oxalic acid dihydrate, 12′, there are two hydrogen bonds from the water molecule which were not distinguished by the NMR measurements as a result of a rapid-flip motion of the water molecules which averaged the two tensors into one.

(8) The hydrogen bonding in $Ca(OH)_2$, if it exists, is a very weak symmetrical three-center bond.

The results

The correlations between the hydrogen-bond lengths and $\bar{\sigma}$ and $\Delta\sigma$ are shown in Figs. 1 and 2. In Fig. 1(*a*), we have plotted all the data from Table 1. In Fig. 1(*b*), we have plotted only the neutron data, and have taken the following liberties: moved 1 to 1·30 Å; interchanged 6 and 6′; and omitted 20 and 21.

In view of the caveats concerning the structural data, the resulting points fit surprisingly well to a

Table 1. *Chemical shifts versus hydrogen-bond distances and angles for some single crystals*

The NMR and crystallographic references are the same as those reported by Berglund & Vaughan (1980), except where noted otherwise. $\bar{\sigma}(\mathrm{TMS}) = 1/3(\sigma_{11}+\sigma_{22}+\sigma_{33})$. $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. $\sigma_{\parallel}$ is the major axis of the tensor ellipsoid, approximately parallel to the hydrogen bond; $\sigma_{\perp}$ is the mean of the other axes.

Compound	Method *X* or *N*	H···O (Å)	O–H···O (°)	$\bar{\sigma}$(TMS) (p.p.m.)	$\Delta\sigma$ (p.p.m.)
H-Bonded anions					
1 KH malonate	*N*	1·234 (3)	180·0	−20·5	27·6
2 NH_4H_2 phosphate	*X*	1·24	180	−19·7	36·0
3 KH oxydiacetate	*N*	1·328 (3)	174·2 (3)	−19·6	28·3
4 KH dicrotonate	*N*	1·348 (2)	178·0 (3)	−18·2	28·9
5 KH_2 phosphate	*N*	1·410 (4)	177·7 (4)	−17·4	37·0
6 KH_3 selenate	*N*	1·529 (6)	171·1 (4)	−13·7	31·5
6′		1·575 (3)	175·2 (2)	−14·7	34·5
7 KH carbonate	*N*	1·587 (2)	172·6 (1)	−16·1	26·7
8 NH_4H oxalate.0·5H_2O	*X*	1·59	175	−14·0	22·0
9 KH sulfate	*X*	1·60	174	−14·5	27·3
9′		1·66	170	−12·7	24·2
10 KH phthalate	*X*	1·70	143	−14·0	30·0
Carboxylic acids					
11 Squaric acid	*N*	1·475 (9)	175·3 (9)	−15·3	24·4
12 α-Oxalic acid.2H_2O	*N*	1·480 (7)	179·3 (9)	−16·6	29·6
13 Maleic acid	*X*	1·54	171	−16·6	22·7
13′		1·67	178	−14·5	19·0
14 Trichloroacetic acid	*N*	1·658 (9)	176·5 (5)	−13·9	20·0
15 Pyromellitic acid.2H_2O	*X*	1·61	160	−15.0	26·4
15′		1·72	171	−12·2	17·4
16 Anhydrous oxalic acid	*X*	1·85	145	−12·6	16·6
Inorganic acid					
17 α-Selenous acid	*N*	1·621 (3)	170·6 (3)	−12	24·0
17′		1·749 (3)	153 (3)	−9	21·0
Hydrates					
18 $MgSO_4.H_2O$	*N*	1·810 (10)	158·4 (11)	−9·3	19·6
8′ NH_4 H oxalate.0·5H_2O	*X*	1·84	161	−5·3	—
19 $CaSO_4.2H_2O$	*N*	1·879 (27)	171·6 (20)	−9·3	—
15″ Pyromellitic acid.2H_2O	*X*	1·91	160	−6·0	—
12′ α-Oxalic acid.2H_2O	*N*	1·917 (8) 1·979 (9)	166·9 (6) 156·6 (7)	−8·2	—
20 Ice I*h*	*N*	1·736	~180	−8·3	28·5
21 $Ca(OH)_2$	*N*	2·645 (2)	128·5 (2)	−4·6	14·0

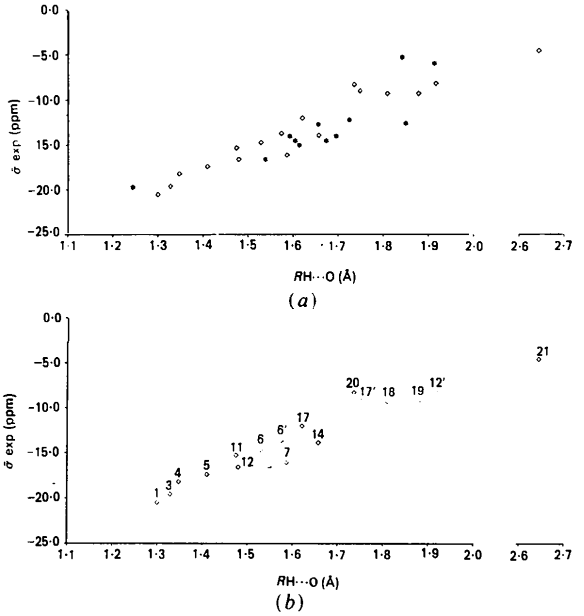

Fig. 1. (*a*) $\bar{\sigma}$ *versus* *R*H···O for all data (◇: neutron data; ∗: X-ray data). (*b*) $\bar{\sigma}$ *versus* *R*H···O for neutron data.

linear plot of −20 p.p.m. for $\bar{\sigma}$(TMS) per 1·0 Å in H···O bond length. The slope is closer to that of the theoretical points, based on *ab initio* calculations of the *R*OH and *R*COOH dimers, than the experimental in the correlation between $\bar{\sigma}$ and O···O separations reported in the earlier publication (Berglund & Vaughan, 1980).

There is certainly no evidence that the relationship between hydrogen-bond length and the trace of the

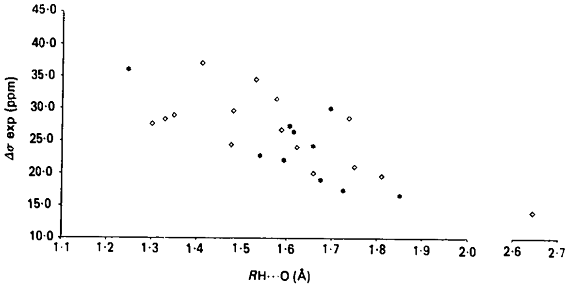

Fig. 2. Δσ *versus* *R*H···O (◇: neutron data, ∗: X-ray data).

proton anisotropic chemical shift is other than linear over the whole range, from very short almost symmetrical bonds to long hydration bonds.

The X-ray data, with one exception, lie on or systematically below the line correlating the neutron data. In correcting the hydrogen positions for the X-ray shortening effect, we used a standard O–H covalent bond length of 0·97 Å. For the shorter hydrogen bonds in the range 1·5 to 1·7 Å, the O–H covalent bond lengths are longer because of the correlation between O–H and H···O bond lengths. Corrections of 1·02 to 0·98 Å are more appropriate. This would move the six X-ray data in the range 1·58 to 1·72 Å closer to the line by 0·05 to 0·01 Å.

Of the neutron analyses, only three were carried out at liquid-nitrogen temperatures, and only for $Ca(OH)_2$ and ice were corrections made for the effects of thermal anharmonicity on the motion of the hydrogen atom relative to the oxygen atom to which it is covalently bonded. These corrections are significant, even at very low temperatures, ~15 K, and can affect hydrogen-bond lengths by as much as 0·04 Å (Craven & Swaminathan, 1984; Jeffrey & Ruble, 1984).

It is clear from these data that well coordinated proton NMR and single-crystal neutron diffraction measurements at low temperatures (~10 K) could establish a very precise experimental relationship between the trace $\bar{\sigma}$ and the H···O hydrogen-bond length, against which future theoretical calculations could be tested.

The correlations between the chemical-shift anisotropy, $\Delta\sigma$, and the hydrogen-bond lengths, shown in Fig. 2, have much more scatter, although there is a definite trend for the anisotropy to increase with the stronger bonds. We could find no correlation between the anisotropies and the O–H···O angles.

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References

BERGLUND, B. & VAUGHAN, R. W. (1980). *J. Chem. Phys.* **73**, 2037-2043.

CRAVEN, B. M. & SWAMINATHAN, S. (1984). *Trans. Am. Crystallogr. Assoc.* **20**, 133-135.

DITCHFIELD, R. (1976). *J. Chem. Phys.* **65**, 3123-3129.

FALK, M. & GIGUERE, P. A. (1958). *Can. J. Chem.* **36**, 1680-1685.

FYFE, C. A. (1983). *Solid State NMR for Chemists.* Guelph, Canada: GEC Press.

JEFFREY, G. A. & RUBLE, J. R. (1984). *Trans. Am. Crystallogr. Assoc.* **20**, 129-132.

JEFFREY, G. A., WOOD, R. A., PFEFFER, P. E. & HICKS, K. B. (1983). *J. Am. Chem. Soc.* **106**, 2128-2133.

KENNEDY, N. S. J., NELMES, R. J., THORNLEY, F. R. & ROUSE, K. D. (1976). *Ferroelectrics*, **14**, 591-593.

MEHRING, M. (1983). *Principles of High Resolution NMR in Solids.* Berlin: Springer-Verlag.

ROHLFING, C. M., ALLEN, L. C. & DITCHFIELD, R. (1983). *J. Chem. Phys.* **79**, 4958-4966.

TAYLOR, M. G., MARCHESSAULT, R. H., PEREZ, S., STEPHENSON, P. J. & FYFE, C. A. (1985). *Can. J. Chem.* **63**, 270-273.

TAYLOR, R. & KENNARD, O. (1983). *Acta Cryst.* **B39**, 133-138.

International Union of Crystallography

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Structure Reports

Volume 48*B* of *Structure Reports* has recently been published. It is in two parts (vi+772 and vi+1080 pages) and covers the literature for organic compounds (including organometallic compounds) for 1981. The price of the new volume is 510 Netherlands guilders for subscribers with standing orders. The full price for individual copies is 600 guilders but personal subscribers may buy a copy for their own use at 300 guilders. Orders for this publication may be placed direct with the publishers, D. Reidel Publishing Company, PO Box 17, 3300 AA Dordrecht, The Netherlands, with Polycrystal Book Service, PO Box 27, Western Springs, IL 60558, USA, or with any bookseller.

The last volume published in this series was Volume 46*B*, for 1980. Volume 47*B* will be the cumulative index for the years 1971-1980 inclusive.

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International Union of Crystallography announces the Ewald Prize

The International Union of Crystallography announces the establishment of the Ewald Prize for outstanding contributions to the science of crystallography. The name of the prize has been chosen with the kind consent of the late Paul Peter Ewald, to recognize Professor Ewald's significant contributions to the foundations of crystallography and to the founding of the International Union of Crystallography, especially his services as the President of the Provisional International Crystallographic Committee from 1946 to 1948, as the first Editor of the Union's publication *Acta Crystallographica* from 1948 to 1959, and as the President of the Union from 1960 to 1963.

The prize consists of a medal, a certificate and a financial award. It will be presented once every three years during