The fact that these hydroxyl groups do not form hydrogen bonds between the naphthyl groups I and II, should be responsible for the repulsive forces between them, which, together with the repulsions between C(9)H and C(9′)H, would account for the larger twist angle between the two groups.

Two projections of the crystal structure along the *b* axis and the *c* axis are shown in Figs. 5(*a*) and (*b*). In these Figures, intermolecular short distances of less than 3·8 Å are shown. It is seen that the closest contacts of the molecules take place mainly between the atoms in the substituents (hydroxyl and methoxycarbonyl groups) and those in the naphthyl groups of the neighbouring molecules related by a twofold screw axis. The shortest distances are, 3·18 Å between C(12′) (methyl carbon) and O(1′) (hydroxyl oxygen), 3·25 Å between C(7) (ring carbon) and O(1) (hydroxyl oxygen) and 3·26 Å between C(7′) and O(1′).

The binaphthyl groups are packed together chiefly through these contacts to form a sheet parallel to (100). The packing of the sheets is conditioned mainly by the interactions among the methoxycarbonyl groups of the group II and those between the atoms of bromobenzene and group II. The molecules of bromobenzene are enclosed in the structure as a solvent of crystallization. It is seen in Fig. 5(*a*) that these molecules are arranged mutually antiparallel along the twofold screw axis and fill up the spaces between the sheets of the binaphthyl groups. Several close contacts of about 3·7 Å hold the bromobenzene molecules in their positions, the shortest distance being 3·38 Å which is found between C(3″) and C(12) (methyl carbon).

The authors wish to express their sincere thanks to Professor Shun-ichi Yamada for his suggestion of the problem and continuous encouragement during all stages of this work, and to Dr T. Shioiri for his valuable discussions. We also wish to express our thanks to C. Itoh Electronic Computing Service for use of an CDC 3600 computer.

References

AKIMOTO, H., SHIOIRI, T., IITAKA, Y. & YAMADA, S. (1968). *Tetrahedron Letters*, **97**.

ALMENNINGEN, A. & BASTIANSSEN, O. (1958). *Kgl. Norske Videnskab. Selskabs Skrifter*, No. **4**, 1.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BERTINOTTI, F., GIACOMELLO, G. & LIQUORI, A. M. (1954). *Acta Cryst.* **7**, 808.

COCHRAN, W. (1953). *Acta Cryst.* **6**, 260

CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504.

ELIEL, E. L. (1962). *Stereo Chemistry of Carbon Compounds.* New York: McGraw-Hill.

FARAG, M. S. (1954). *Acta Cryst.* **7**, 117.

International Tables for X-ray Crystallography (1962). Vol. III, p. 214. Birmingham: Kynoch Press.

HARGREAVES, A. & HASAN RIZVI, S. (1962). *Acta Cryst.* **15**, 365.

MISLOW, K. (1958). *Angew. Chem.* **70**, 683.

OKAYA, Y. & ASHIDA, T. (1967). *HBLS IV, The Universal Crystallographic Computing System* (I), p. 65. Japanese Crystallographic Association.

ROBERTSON, J. M. (1936). *Proc. Roy. Soc.* A**167**, 122.

ROBERTSON, J. M. & UBBELOHDE, A. R. (1938). *Proc. Roy. Soc.* A**167**, 122.

ROBINSON, B. & HARGREAVES, A. (1964). *Acta Cryst.* **17**, 944.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.

WATSON, H. C. & HARGREAVES, A. (1958). *Acta Cryst.* **11**, 556.

Acta Cryst. (1969). B**25**, 1500

Proton Magnetic Resonance Study of Zinc Benzenesulphonate Hexahydrate

BY G. RANGARAJAN AND J. RAMAKRISHNA

Department of Physics, Indian Institute of Science, Bangalore 12, India

(*Received* 23 *April* 1968 *and in revised form* 4 *September* 1968)

The lengths and orientations of the interproton vectors of the water molecules in a single crystal of zinc benzenesulphonate hexahydrate have been determined by the Pake (*J. Chem. Phys.* (1948) **16**, 237) method with use of proton magnetic resonance. The proton–proton distance in all the water molecules is 1·61 ± 0·03 Å. An attempt has been made to locate the protons by use of the hydrogen-bonding schemes suggested by the X-ray workers Broomhead & Nicol (*Acta Cryst.* (1948) **1**, 88), but the interproton vectors and the lines joining the acceptor oxygen atoms are not found to be parallel, though the bonds are of normal length. Alternative hydrogen-bonding schemes considered have acceptor oxygen atoms such that the bond lengths are too large, though the parallelism is reasonably good. A refinement of the crystal structure is probably necessary to fix the correct hydrogen bonding schemes.

Introduction

Water molecules in hydrated crystals are typical two-spin systems, in which the intramolecular proton–proton vector can be unambiguously determined, by use of the Pake (1948) method. Following Pake, the splitting of the resonance lines due to the dipolar interaction between the protons is given by:

$$\Delta H = 2\alpha[3 \cos^2 \delta \cos^2 (\varphi - \varphi_0) - 1] . \qquad (1)$$

The parameters α, φ_0 and δ completely specify the length and the orientation of the proton–proton (p–p) vector in the unit cell.

As part of a general program of study of hydrated crystals, we have investigated the proton magnetic resonance in zinc benzenesulphonate hexahydrate, $Zn(C_6H_5SO_3)_2.6H_2O$, and the results are presented in this paper. The X-ray analysis of the crystal structure was carried out by Broomhead & Nicol (1948), according to whom there is extensive hydrogen bonding in this crystal.

The crystal belongs to the monoclinic space group $P2_1/n$ and there are two molecules in the unit cell. The unit-cell dimensions are $a = 22{\cdot}54$ Å, $b = 6{\cdot}32$ Å, $c = 6{\cdot}98$ Å, $\beta = 93°36'$. The crystallographically equivalent positions are given by:

$$\pm(x,y,z);\ (\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z)\,,$$

with the zinc atoms occupying centres of symmetry, (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

Since there are twelve water molecules in the unit cell, from the point of view of a proton magnetic resonance experiment, there are three non-equivalent (p–p) vectors in the unit cell, when the crystal is rotated about the b axis, with the magnetic field in the *ac* plane.

An aqueous solution of zinc benzenesulphonate was prepared by adding zinc sulphate to an aqueous solution of barium benzenesulphonate and filtering off the white barium sulphate precipitate. The filtrate, on slow evaporation, gave good single crystals of zinc benzenesulphonate with six water molecules of hydration. The density of $1{\cdot}58$ g.cm^{-3}, as measured by the flotation method, was in agreement with the value of $1{\cdot}577$ g.cm^{-3}, calculated by assuming two molecules per unit cell.

The crystals were thick and had a square cross-section. The crystal used in our experiments had the dimensions 1 cm × 1 cm × 0·6 cm.

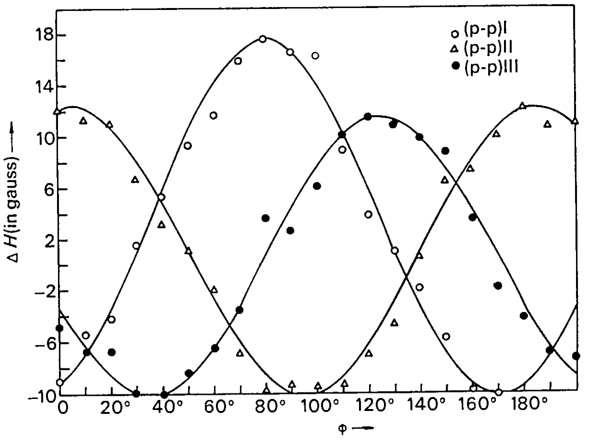

Fig. 1. Pake curves for b axis rotation of zinc benzenesulphonate hexahydrate.

Experimental

The measurements were made at room temperature, by use of a modified PKW type nuclear magnetic resonance spectrometer working at 14 Mc.sec^{-1}. We used a modulation of about 1 gauss at 330 c.p.s. and a sweep rate of 0·047 gauss sec^{-1}. The n.m.r. derivative signals were recorded with a Varian G11A recorder. The signal to noise ratio was greater than 10. The crystal was rotated about the b axis and the signals were recorded for 18 orientations at intervals of 10° each.

All the experimental curves had a central peak due to protons of benzene group. To determine the shape and amplitude of this signal, a second crystal of almost identical size was dehydrated by baking it in an oven at a temperature of about 120 °C for over 24 hours, and the powder spectrum of this dehydrated sample matched the experimental curves in signal strength as well as in shape, wherever the water–proton doublets had separated out enough to make such a comparison meaningful. A standard derivative curve was also prepared for the water–proton resonance, from the best resolved spectrum. The width of the standard derivative curve was about 3·3 gauss. Three such pairs of derivative curves were used in conjunction with the central signal to resolve the experimental derivative curves and obtain the values of ΔH. ΔH was measured as the separation between positions of maximum intensity between the pairs of derivatives corresponding to each of the three p–p vectors. The assignment of these values to the three (p–p) vectors was done by remembering that ΔH has a minimum value of -2α at $(\varphi-\varphi_0) = 90°$, which, for proton pairs in hydrates ranges from -10 to -11 gauss, and a maximum value of $2\alpha(3\cos^2\delta - 1)$ when $\varphi = \varphi_0$. In the present case, since we have three inequivalent (p–p) vectors, there should be three such maxima and minima in the experimental ΔH values, with a separation of 90° between each maximum and the corresponding minimum. Once these maxima and minima are located, α, φ_0 and δ for each (p–p) vector can be estimated from the relations:

$$\Delta H_{\min} = -2\alpha\,;$$

$$\Delta H_{\max} = 2\alpha(3\cos^2\delta - 1) \text{ at } \varphi = \varphi_0\,.$$

With these values the theoretical Pake curves for the three (p–p) vectors were plotted and values of ΔH lying close to each curve were assigned to one (p–p) vector. Considerable care should, however, be taken in this process.

Through suitable small variations in these values of α, φ_0 and δ, a satisfactory visual fit of the experimental points with the theoretical curves was accomplished; this fit was then improved by the method of least-squares and this gave us the final set of values for α, φ_0 and δ.

Results and discussion

The results of the analysis are shown in Fig. 1. We obtained a value of 10·1 gauss for 2α, corresponding to an interproton distance of 1·61 Å, the experimental error being within 0·03 Å. The φ_0 and δ values for the three (p–p) vectors are given in Table 1.

Table 1. *Orientations of the three (p–p) vectors in zinc benzenesulphonate hexahydrate (φ was taken to be* 0° *when the magnetic field was parallel to the a axis)*

	φ_0	δ
(p–p) I	82°	17°
(p–p) II	7	31
(p–p) III	127	32

The accuracy in these angles is limited mainly by the accuracy with which the spectra were resolved and, in the present case, it is of the order of 5°.

According to the X-ray structure analysis, all the water-protons are involved in hydrogen bonding. In the following, we adopt the symbols given by Broomhead & Nicol for the various atoms. The projection of the crystal structure on the *ac* plane is shown in Fig. 2. According to them, the water molecule $(H_2O)_1$ is involved in hydrogen bonding with the oxygen atoms $_tO_2$ and $_tO_3$, $(H_2O)_2$, with $_tO_1$ and $_tO_2$ and $(H_2O)_3$, with $_tO_1$ and $_tO_3$. The distances between the water oxygen and the acceptor oxygen atoms all lie in the range between 2·72 and 2·86 Å.

An infrared study of the crystal revealed a shift of about 300 cm^{-1} for the O–H stretching frequency, confirming the presence of hydrogen bonding in the structure.

In a proton magnetic resonance experiment, only the length and the orientation of the (p–p) vector are determined. It is generally found, however, that the protons of the water molecules in hydrates participate in hydrogen bonding with the nearest electro-negative atoms. The (p–p) vector and the line joining the two acceptor atoms are then expected, and generally observed to be, approximately parallel, especially in situations where the bonds are of normal length and are not bent.

The angles φ_0 and δ were, therefore, calculated for the various O–O lines which involve the acceptor oxygen atoms suggested by the X-ray workers (φ_0 and δ carry the same significance as for the p–p line), and these values are given in Table 2.

Table 2. *Orientations of the O–O lines which involve the acceptor oxygen atoms suggested by the X-ray study*

H-bonding scheme	φ_0	δ
$_tO_2$–$O_{(H_2O)_1}$–$_tO_3$	84°	0°
$_tO_1$–$O_{(H_2O)_2}$–$_tO_3$	96	74
$_tO_1$–$O_{(H_2O)_3}$–$_tO_2$	84	73

A comparison between Table 1 and Table 2 shows that only for $(H_2O)_1$, is there some agreement between the angles. Even here, the discrepancy in δ is 17°. Besides, if δ were zero as suggested by Table 2, $(\Delta H_{\max}/\Delta H_{\min})$ should be exactly equal to 2, but this is not the case, as revealed by our experiment.

Considering the (p–p) vectors belonging to $(H_2O)_2$ and $(H_2O)_3$, Table 2 suggests that the δ values should be around 70° in both cases, if the (p–p) vector were parallel to the O–O line. From the Pake equation we can see that if δ were greater than 54°44′, the doublet separation should never cross zero and take positive values, but we find, however, that the ΔH values in these cases do reach positive values.

We therefore looked for other possible acceptor atoms around $(H_2O)_2$ and $(H_2O)_3$ which might lead to more satisfactory values for φ_0 and δ; the only hydrogen bonding schemes we could find were:

$$O_1\text{–}(H_2O)_2\text{–}{}_tO_1$$

and

$$_tO_1\text{–}(H_2O)_3\text{–}O_3$$

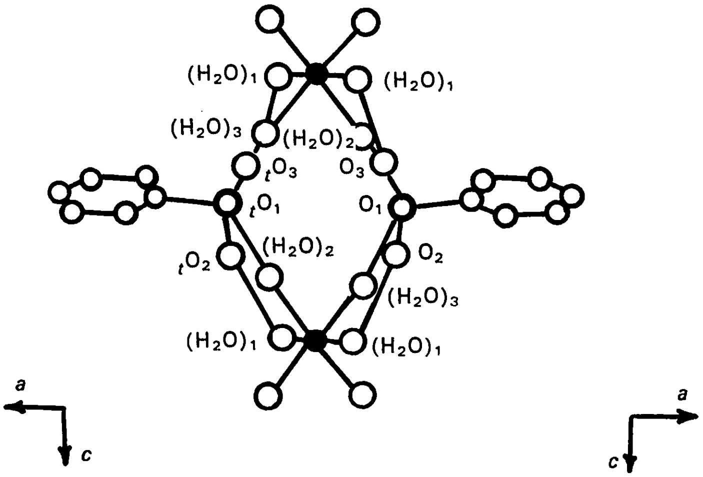

Fig. 2. Projection of the structure of zinc benzenesulphonate hexahydrate on the *ac* plane. Only oxygen atoms have been indicated.

leading to values of φ_0 and δ for the O–O lines shown in Table 3.

Table 3. *Orientations of the* O–O *lines which involve acceptor oxygen atoms different from those suggested in the X-ray work*

H-bonding scheme	φ	δ
O_1–$(H_2O)_2$–ιO_1	26°	23°
ιO_1–$(H_2O)_3$–O_3	150	45

Though these values are in better agreement with the experimental values for (p–p)II and (p–p)III, shown in Table 1, the distances $(H_2O)_2$–O_1 and $(H_2O)_3$–O_3 are rather too large, being about 4 Å.

The angles O–H_2O–O are in the range between 108° and 112° for all the bonding schemes considered here and so this does not provide us with a basis for making a choice.

Conclusions

If the hydrogen bonding scheme suggested by Broomhead & Nicol (1948) is assumed to be correct, we find that the parallelism between the p–p and the O–O lines usually found in hydrates is not present here, even though the bond lengths are normal. Alternatively the hydrogen bonding schemes suggested by them are not the right ones and we have to look for other acceptors in the structure.

The only other set of acceptor atoms we could find is such that the bond lengths are too large, even though the parallelism between the p–p and the O–O lines is fairly reasonable.

The difficulty encountered in fixing the hydrogen bonding schemes is probably a result of the fact that the accuracy of the X-ray work is rather poor. We feel that a refinement of the structure will help to fix the hydrogen-bonded atoms and hence the proton positions.

We are deeply indebted to Professor R. S. Krishnan for his kind interest and to Professor P. S. Narayanan for supplying the infrared results.

References

Broomhead, J. M. & Nicol, A. D. I. (1948). *Acta Cryst.* **1**, 88.
Pake, G. E. (1948). *J. Chem. Phys.* **16**, 237.

Acta Cryst. (1969). B**25**, 1503

The Albite Structures

By P. H. Ribbe*, Helen D. Megaw and W. H. Taylor
Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England
[An analysis based on experimental measurements
by R. B. Ferguson
Department of Geology, University of Manitoba, Winnipeg, Canada
and R. J. Traill
Geological Survey of Canada, Ottawa, Canada]

(*Received* 6 *May* 1968)

Three-dimensional analyses of the low albite and high albite studied by Ferguson, Traill & Taylor in 1958 have confirmed that in the low temperature material the Al, Si distribution is highly ordered, in the high temperature almost completely random, and have also confirmed the marked anisotropy of the Na atom in both materials. The improved accuracy has shown that in low albite the sites $T_1(m)$, $T_2(0)$, $T_2(m)$ are almost free of Al, whereas the earlier analysis required the allocation of a small amount of Al to $T_2(0)$. The observed anisotropy of the Na atom in low albite may be interpreted in terms of a multipartite structure with faulted domains, though an explanation in terms of anisotropic thermal vibration is more probable. For high albite the very large anisotropy of the Na atom, and the diffuse nature of the atomic peaks of electron density, point to the interpretation of the diffraction pattern as representing only an average structure; in this material the evidence for a multipartite structure with faulted domains is considerably stronger than for low albite.

An Appendix compares the effects of temperature factor with those of 'splitting' of atoms.

1. Introduction

The first examination of the structure of (low) albite, $NaAlSi_3O_8$ (Taylor, Darbyshire & Strunz, 1934), which established its relationship to other felspar structures, was followed in 1958 by two-dimensional analyses of low albite and high albite by Ferguson, Traill & Taylor. These analyses showed that in low albite the Al, Si distribution is highly ordered whereas in high albite it is random or very nearly so. They also revealed the markedly anisotropic character of the Na atom, which

---

* Present address: Department of Geological Sciences, Virginia Polytechnic Institute, Blacksburg, Virginia, U.S.A.