

ences appear in most cases at the third significant figure. A noticeable feature is that the four structures have not revealed any marked anisotropy of the atomic vibrations and, furthermore, there is no preferred vibrational direction taken collectively for the ellipsoids.

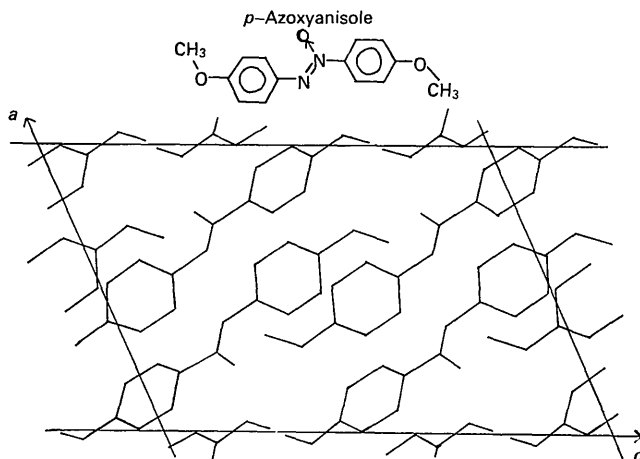


Fig. 1. Projection on (010) of *p*-azoxyanisole molecules.

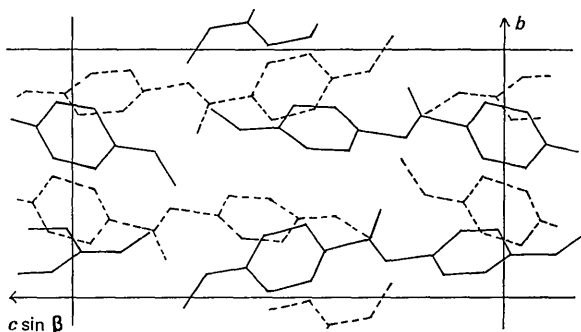


Fig. 2. Projection down the *a* axis of *p*-azoxyanisole.

We undertook this structure determination primarily to see if any light could be thrown on the nature of the meso-phases of the material. While the molecules pack in an imbricated manner, as originally pointed out by Bernal & Crowfoot (1933), this observation alone, which has now been confirmed, does not by itself explain why the crystals should go through the nematic phase on heating. At the time of the preparation of our abstract for the I.U.Cr. Congress, it was thought that there was some evidence of disorder in the structure, but further work cast doubts on this view. Furthermore, the low *R* values for the independent structure determinations tend, if anything, to throw less light on this problem. Hence the 'smears' connecting the X-ray reflexions in the X-ray diffraction patterns, as originally noticed by Bernal & Crowfoot and confirmed by us and by Krigbaum *et al.* and by Braun *et al.* need more careful evaluations both from the kinematic and dynamical points of view. We have found this effect to be very marked in the case of our crystals of *p*-azoxyphenetole. Fig. 3(*a*) and (*b*) show for comparison the 'smear' effects observed in the diffraction patterns of the two crystals.

Work is now proceeding on the structure determination of the phenetole compound whose molecules also pack in an imbricated manner, as shown from preliminary investigations (Smith, 1969).

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The water molecules in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. By Z. M. EL SAFFAR and WILLIAM MULCAHY, *Department of Physics, De Paul University, Chicago, Illinois 60614, U.S.A.*

(Received 10 December 1970)

Proton magnetic resonance line shapes of polycrystalline $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ have been fitted with least-squares to a line-shape function containing a variable parameter dependent on the H–H distance of the water molecule. The H–H distance corresponding to the best fit is found to be 1.59 ± 0.01 Å in disagreement with the value 1.70 Å reported by Buchanan & Harris using neutron diffraction.

The structure of aluminum chloride hexahydrate has been studied with X-ray and neutron diffraction techniques by Buchanan & Harris (1968). The dimensions of the hexagonal unit cell were given as *a*, *c* = 11.827, 11.895 Å with $R\bar{3}c$ space group symmetry and *Z* = 6. The six water molecules surround a central aluminum ion forming an essentially regular close-packed octahedron. The two hydrogen atoms associated with a given oxygen atom form normal hydrogen bonds to the nearest-neighbor chlorine ions at

3.02 and 3.03 Å from oxygen. The H–H distance of the water molecule was reported by Buchanan & Harris to be 1.70 Å. This rather high value of the H–H distance attracted our attention.

All thirty-six water molecules in the unit cell of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are structurally equivalent. This makes $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ particularly suitable for a simple proton magnetic resonance (p.m.r.) study in the polycrystalline form. The technique involves fitting the shape of the ob-

served resonance spectrum to a theoretical lineshape function first given by Pake (1948). This technique has recently been utilized and described in detail by Pedersen (1968).

The shape of the first derivative of the absorption spectrum is given by

$$F(h) = \int_{-\infty}^{\infty} (h-h')[g(h')+f(h')] \exp[-(h-h')^2/2\beta^2] dh' \quad (1)$$

where $g(h')$ is given by $(1-h'/\alpha)^{-1/2}$ in its non-zero range from -2α to $+\alpha$ and $f(h')$ is given by $(1+h'/\alpha)^{-1/2}$ in its non-zero range from $-\alpha$ to $+2\alpha$. The variable parameters to be determined are α and β where

$$\alpha = \frac{3\mu}{2R^3} \quad (2)$$

and

$$\beta^2 = \frac{9}{5} \mu^2 \sum_i r_i^{-6} + \frac{4}{15} \sum_k \mu_k^2 \frac{I_{k+1}}{I_k} r_k^{-6}. \quad (3)$$

Here μ is the magnetic moment of the proton, R is the H-H distance, r_i is the internuclear distance between any two protons not in the same pair and, r_k is the distance between one proton and any other nucleus in the structure carrying a magnetic moment μ_k and spin I_k . The above definitions of α and β assume the absence of significant molecular motion such as 180° flips of the water molecules.

Four of the many resonance spectra obtained at room temperature were fitted to the theoretical line-shape function using a general Fortran least-squares program *ORGLS* written by Busing & Levy (1962) (Fig. 1). The average value of α is found to be 5.25 ± 0.1 gauss. This gives a value of 1.59 ± 0.01 Å for the H-H distance which is not unlike other values of the H-H distance obtained by p.m.r. in hydrates (El Saffar, 1966). The average value of β is found to be 2.6 ± 0.1 gauss which is in agreement with the value 2.41 gauss calculated from equation (3) using the structure of Buchanan & Harris. Our assumption concerning the

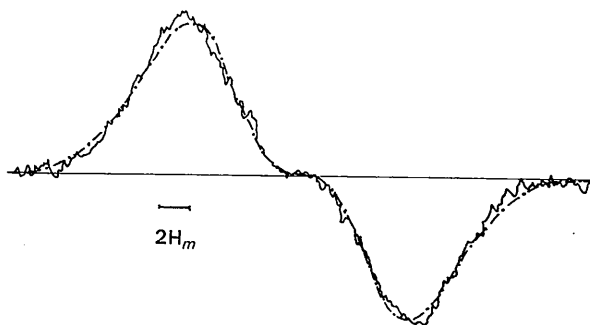


Fig. 1. The observed line shape (solid line) and the theoretical line shape (broken line) fitted by the method of least-squares. $2H_m$ stands for the peak-peak modulation.

absence of twofold motion of the water molecules at room temperature was confirmed by spin-lattice relaxation measurements (El Saffar, Mulcahy & Rochau, 1971).

In conclusion it appears that neutron diffraction studies utilizing a limited number of reflections such as the one reported by Buchanan & Harris (1968) should be viewed with caution.

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Acta Cryst. (1971). B27, 1070

The crystal structure of K_2SeO_4 . By A. KÁLMÁN, J. S. STEPHENS and D. W. J. CRUICKSHANK, *Department of Chemistry, U.M.I.S.T., Manchester M60 1QD, England*

(Received 17 February 1971)

An addendum to *Acta Cryst.* (1970) B26, 1451.

In our paper (Kálmán, Stephens & Cruickshank, 1970) on K_2SeO_4 we referred to 'a slight but systematic error in the geometry of the (Hilger & Watts) four-circle goniometer'. We regret that we did not make it clear that this slight fault was due to accidental disturbance of the alignment of the

instrument, which had not been corrected at the time of use.

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