

Fig. 3 illustrates two closely stacked PAAB molecules, viewed from a direction perpendicular to the mean molecular planes. Each azo group is sandwiched between two benzene rings, and each central benzene ring is between two azo groups. A similar stacking of aromatic rings and double bonds was reported in the crystal structure of the naphthalene-tetracyanoethylene complex (Williams & Wallwork, 1967), and several other examples involving dipolar molecules are discussed by Prout & Wallwork (1966).

The crystal structure of PAAB shows little resemblance to that reported for *trans*-azobenzene (Brown, 1966). There are two crystallographically independent half-molecules in the asymmetric unit of *trans*-azobenzene; one of these was found to be ordered, and the other probably disordered. The bond distances and angles found for the ordered molecule of *trans*-azobenzene differ insignificantly from the corresponding values reported here for PAAB. However, the *trans*-azobenzene molecule is nonplanar; there is a torsion of 17.1° about the bond connecting the benzene ring and the azo group in the ordered molecule. Moreover, there is a striking difference in the packing. No intermolecular contacts (involving C or N atoms) less than 3.63 \AA

are reported for *trans*-azobenzene. In PAAB, every atom is within 3.6 \AA of atoms in at least one other PAAB molecule.

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The use of a polarized hydrogen atom in X-ray structure refinement.* By PHILIP COPPENS, *Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214, U.S.A.*

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A one-center polarized hydrogen atom formalism has been tested in the routine refinement of a number of crystal structures. The effect on the bond lengths involving hydrogen atoms, and the interaction between anisotropic thermal motion and form factor asymmetry, are discussed.

It is well known that X-H bond lengths ($X=C, N, O$) as determined by X-ray diffraction are shortened, because an appreciable part of the charge on the hydrogen atom is displaced towards the bond center. As the shortening of the X-H bonds is, to a large extent, the result of an incorrect scattering formalism rather than an inherent property of the X-ray data, it is of interest to examine if an improved nonspherical formalism can correct the effect. In principle, such a formalism should include a two-center term describing the bond density (Stewart, 1969; Coppens, Csonka & Willoughby, 1971), but a one-center model in which a hydrogen atom is polarized towards the X atom may be adequate for a correction of the bond length. Such a model, based on earlier quantum-mechanical calculations (Rosen 1931), has been described by Hirshfeld & Rabinovich (1967). The hydrogen wave function is described as a mixing of $1s$ and $2p$ orbitals (μ =mixing coefficient), the positive lobe of the p orbital being directed along the H-X bond:

$$\varphi_{\text{H}} = [\varphi(1s) + \mu\varphi(2p)] / (1 + \mu^2)^{1/2} \quad (1)$$

in which $\varphi(1s) = N(1s) \exp(-\lambda r/a_0)$ and $\varphi(2p) = N(2p)z \exp(-\lambda r/a_0)$ (λ =orbital coefficient, N =normalization factor, a_0 =Bohr radius, r =distance from the hydrogen nucleus,

$z=r$ projected along H-X). The corresponding scattering formalism (Hirshfeld & Rabinovich, 1967) has been applied in a modification of our least-squares program, to determine whether bond lengths compatible with those from other techniques can be obtained with suitable values for μ and λ .

The equations used are as follows. If $f(\text{H}) = f' + if''$, with f' and f'' as given by Hirshfeld & Rabinovich, the contributions of the hydrogen atom scattering to the structure factor $F = A + iB$ are:

$$A_{hkl}(\text{H}) = \sum_n \sum_s \{ [a_n f' \cos 2\pi(hx_{ns} + ky_{ns} + lz_{ns}) - a_n f'' \sin 2\pi(hx_{ns} + ky_{ns} + lz_{ns})] T_{ns} \}$$

and

$$B_{hkl}(\text{H}) = \sum_n \sum_s \{ [a_n f' \sin 2\pi(hx_{ns} + ky_{ns} + lz_{ns}) + a_n f'' \cos 2\pi(hx_{ns} + ky_{ns} + lz_{ns})] T_{ns} \}, \quad (2)$$

where the summation is over all n hydrogen atoms in the asymmetric unit and over all s symmetry equivalent position, and a_n and T_{ns} are occupancy and temperature factors, respectively.

For the calculation of the derivatives, it should be noted that f' and f'' depend on the angle between the reciprocal lattice vector hkl and the axis of the p orbital on the

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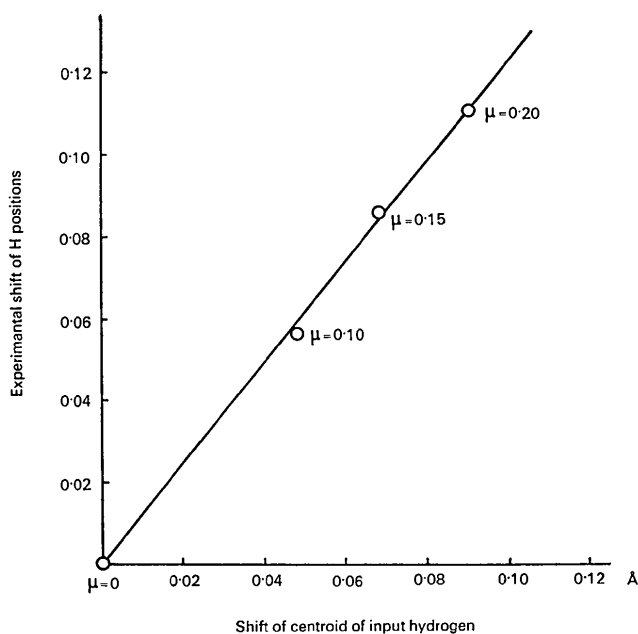


Fig. 1. Average shift of the hydrogen atoms in oxalic acid dihydrate, as a function of the displacement of the centroid of the polarized hydrogen atom.

hydrogen atom. It follows that derivatives such as $\partial f'/\partial x_H$ and $\partial f'/\partial x_x$ are generally non-zero, and consequently additional terms are introduced in the expressions for the structure factor derivatives. However, these terms are very small when the polarized hydrogen atom formalism is introduced after completion of the spherical refinement, because the *direction* of the X-H bond is not altered by the formalism, though the X-H bond length will generally increase. With this simplification, the expression for the derivative $\partial A/\partial x_h$ becomes

$$\frac{\partial A}{\partial x_H} = -2\pi \sum_s \{ [h a_H f' \sin 2\pi(hx_{Hs} + ky_{Hs} + lz_{Hs}) + h a_H f'' \cos 2\pi(hx_{Hs} + ky_{Hs} + lz_{Hs})] T_{Hs} \}. \quad (3)$$

Expressions for the other derivatives required for the least-squares treatment are similar and can readily be derived from (2).

Crystals studied include those of deuterio-oxalic acid dihydrate (Delaplane & Ibers, 1969), pyrene-tetracyanoethylene (Larsen, Little & Coppens, to be published), *d*-pyrene (Larsen & Coppens, to be published), and cyanuric acid (Verschoor & Keulen, 1971). The following discussion deals mainly with the first two crystals, which gave typical results.

The dependence of the bond lengths on the orbital coefficient λ was found to be small, when λ is varied in a reasonable range. The contracted value of 1.20 (a.u.)^{-1} ($1 \text{ a.u.} = 0.529 \text{ \AA}$) was selected. It corresponds, approximately, to the contraction in the hydrogen atom as given by Stewart, Davidson & Simpson (1965).

The results for deuterio-oxalic acid dihydrate for various values of μ are given in Table 1. Isotropic temperature factors for hydrogen are used in the refinement. An appreciable lengthening of the X-H bonds with increasing μ is

observed, but the weighted R value indicates that μ should be less than 0.15. At $\mu=0.10$, the bond lengths are still less than the neutron diffraction values given in the last column of Table 1 (Coppens & Sabine, 1969). This is due, at least partly, to thermal shortening affecting the X-ray, but not the neutron diffraction results (Coulson & Thomas, 1971). In Fig. 1, the average experimental shift is plotted against the shift of the centroid of the hydrogen atom as defined by (1). Here, the shift in the hydrogen position is proportional to the shift of the centroid of the hydrogen density, the proportionality factor being about 1.25. For the pyrene-tetracyanoethylene complex (Table 2) the lengthening of the C-H bond for $\mu=0.10$ is again about 0.06 \AA , but the average value of 1.01 \AA differs more from a typical neutron diffraction C(*sp*²)-H bond length ($\sim 1.08 \text{ \AA}$; Kay, Okaya & Cox, 1971) than was the case for the O-H bond lengths in oxalic acid.

Table 1. Results for deuterio oxalic acid dihydrate

$\lambda = 1.2 \text{ a.u.}^{-1}$ OH bond lengths (\AA); $\sigma \sim 0.03 \text{ \AA}$ (refinement on F)

	$\mu=0$	0.1	0.15	0.20	Neutron
CO-H	0.94	1.00	1.03	1.05	1.031
HO-H	0.84	0.90	0.92	0.95	0.954
	0.86	0.92	0.95	0.97	0.954
$R(F)$	2.3	2.3	2.3	2.3	
$R_w(F)$	2.2	2.2	2.3	2.3	

Table 2. Results for the tetracyanoethylene-pyrene complex

C-H bond lengths (\AA); $\sigma \sim 0.03 \text{ \AA}$ (refinement on F^2)

	$\mu=0$	0.10	0.125	0.20
CH(1)	0.96	1.02	1.03	1.07
CH(2)	0.91	0.97	0.97	1.00
CH(6)	0.95	1.01	1.02	1.05
CH(7)	0.95	0.99	1.01	1.04
CH(8)	1.00	1.05	1.06	1.10
$\langle \text{CH} \rangle$	$\langle 0.95 \rangle$	$\langle 1.01 \rangle$	$\langle 1.02 \rangle$	$\langle 1.05 \rangle$
$R(F)$	5.1	5.1	5.1	5.1
$R_w(F)$	3.8	3.8	3.8	3.8
$R(F^2)$	6.2	6.3	6.3	6.4
$R_w(F^2)$	7.4	7.4	7.5	7.5

The results for cyanuric acid indicate an optimum value of $\mu=0.2$, with a corresponding bond lengthening of about 0.09 \AA . The increased shift agrees with the X-ray minus neutron difference maps, which show much larger peaks in the N-H bonds in cyanuric acid than in the oxalic acid O-H bonds (Coppens & Vos, 1971). In all refinements, no significant changes in heavy-atom positions were found.

Finally, introduction of a polarized hydrogen scattering factor in the valence shell occupancy refinement (Coppens, Pautler & Griffin, 1971) leads to a very small increase in the positive charges generally observed on the hydrogen atom. The increase varies from 0.01–0.02 units, which is smaller than the standard deviations in the charges.

Two main conclusions can be drawn from these calculations. First, no improvement in R value is obtained with the improved formalism for the density. We believe that this is due to the anisotropic nature of the hydrogen thermal vibrations, as evidenced by neutron diffraction results

(Johnson, 1970) and by the large difference between $X-H$ stretching and bending vibrational frequencies. A spherical temperature factor corresponds to too large a thermal motion along the bond direction, thereby partly compensating for the deficiency of the spherical atom wave function. The X-ray data do not allow the determination of anisotropic thermal parameters for the hydrogen atoms, but the use of complementary spectroscopic information should lead to a sharper minimum in R as a function of the mixing coefficient μ .

Second, without the introduction of complementary information on the dynamics of the hydrogen atom little can be learned about the details of the hydrogen atom density. Therefore, it is doubtful that calculations with other reasonable nonspherical hydrogen atom formalisms would lead to results differing considerably from those described here.

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The crystal structure of $CsMnBr_3$. By J. GOODYEAR and D. J. KENNEDY, *Department of Physics, University of Hull, England*

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The crystal structure of $CsMnBr_3$, determined from Weissenberg data, is hexagonal with $a=7.609$ (15), $c=6.52$ (5) Å and $Z=2$. Cs, Mn and Br atoms are located at the special positions $2(d)$, $2(a)$ and $6(h)$, respectively, of the space group $P6_3/mmc$, the structure being isomorphous with that of $CsNiCl_3$.

Introduction

Many structures of $CsMCl_3$ compounds, where M denotes a metal ion in the first transition series, have been found to be isomorphous with $CsNiCl_3$ (Tishchenko, 1955), which is hexagonal (space group, $P6_3/mmc$) with $a \approx 7.2$ Å and $c/a \approx 0.82$. Single-crystal studies of $RbNiCl_3$ and $RbNiBr_3$ (Asmussen, Larsen & Soling, 1969) and of $CsMgCl_3$ (McPherson, Kistenmacher & Stucky, 1970) have shown that these compounds also have this structure.

The unit-cell dimensions of the material examined in this work suggested that its structure might be of the $CsNiCl_3$ type; this was assumed at the beginning and the subsequent refinement of the structure proved it to be so.

Experimental

The material was prepared by heating a stoichiometric mixture of $CsBr$ and $MnBr_2$ to a temperature above the melting point in a sealed evacuated silica tube, and then cooling the specimen at about $10^\circ C$ per hr to room temperature. The resulting red crystalline mass was unstable in the presence of water vapour, and single crystals, suitable for X-ray Weissenberg study, were selected in a stream of dry nitrogen and then sealed in Lindemann glass tubes containing P_2O_5 .

The unit-cell dimensions were determined from rotation and Weissenberg photographs taken about the c -axis with $Cu K\alpha$ radiation ($\lambda = 1.5418$ Å). Agreement between the observed and X-ray densities was obtained by assigning two formula units of $CsMnBr_3$ per unit cell. The appropriate crystal data are presented in Table 1.

Table 1. *Crystal data*

Formula, $CsMnCl_3$;	F. W. 427.60
Hexagonal;	$a = 7.609$ (15), $c = 6.52$ (5) Å
	$Z = 2$; $D_o = 4.30$, $D_x = 4.34$ g.cm $^{-3}$
Mean r (cm)	0.0032
μ (cm $^{-1}$)	269 ($\lambda = 0.7107$ Å)

Intensity data were collected from equi-inclination multiple-film Weissenberg photographs taken about the c axis with $Mo K\alpha$ radiation using a crystal of cross-section 0.04×0.08 mm. Reflexions with indices hkl , $l = 2n + 1$, were systematically absent, in keeping with space groups $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. The intensities of about 380 reflexions from layer lines 0 to 5 were measured using a Joyce-Loebl flying-spot microdensitometer; of these about 95 were symmetrically independent. These data were corrected for the Lorentz-polarization factor and for absorption using the correction factors given by Bond (1959) for a cylindrical crystal.

Structure determination

Since $CsMnBr_3$ was expected to be isostructural with $CsNiCl_3$ the atoms were assigned to the following positions in the space group $P6_3/mmc$: Cs at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, Mn at $(0,0,0)$ and Br at $(x, 2x, \frac{1}{2})$. A two-dimensional least-squares refinement of the $hk0$ data was carried out using an initial positional parameter for the bromine atom the same as that of the chlorine atom in the $CsNiCl_3$ structure and the isotropic temperature factors found for Cs_2MnBr_4 by Goodyear, Steigmann & Kennedy (1972). After 10 cycles the reliability