Acta Cryst. (1964). **17**, 415

The Crystal Structure of Perdeuterated Violuric Acid Monohydrate: The Neutron Diffraction Analysis

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(*Received* 24 *April* 1963)

Following the determination of the heavier atom positions in crystals of perdeuterated violuric acid monohydrate (Craven & Mascarenhas*), the deuterium atom positions have been determined by a two-dimensional neutron diffraction analysis. The crystals are orthorhombic, space group $Cmc2_1$, with cell parameters $a=6{\cdot}217\pm0{\cdot}002$, $b=14{\cdot}373\pm0{\cdot}002$, $c=7{\cdot}516\pm0{\cdot}001$ Å and with four molecules per cell. All atoms lie in the crystallographic mirror planes $x=0, \frac{1}{2}$, in a very compact hydrogen bonded layer structure with each water molecule surrounded in a plane by four oxygen atoms which are all at feasible hydrogen bonding distances. The intensities of 67 reflexions $0kl$ were measured, comprising all those observable with neutron wavelength 1·14 Å and $2\theta<80°$. The parameters for the C, N, and O atoms were assumed from the X-ray analysis and the fifteen positional and isotropic thermal parameters were determined for the deuterium atoms by Fourier and least-squares procedures. The hydrogen bonding scheme features a bifurcated bond between the water molecule and two oxygen atoms of the violuric acid molecule. The distances from the shared deuterium to the acceptor oxygens are 2·07 and 2·10 Å. The bond lengths in the D_2O molecule are 0·97 and 0·94 Å with bond angle 106°. The hydroxyimino O–D length is 1·02 Å and the pyrimidine N–D lengths are 0·97 and 1·06 Å. The estimated standard deviation in a bond length involving a deuterium atom is 0·025 Å.

Introduction

Perdeuterated violuric acid monohydrate (5-hydroxyiminobarbituric acid, Fig. 1) is one of a number of hydrates of barbituric acid and its simple derivatives which crystallize in compact hydrogen bonded sheets with a characteristic intersheet separation of about 3·2 Å. These structures (*e.g.* barbituric acid dihydrate, 5-nitrobarbituric acid trihydrate) are of interest because of the apparently coplanar coordination of hydrogen bonding acceptor and donor atoms about the water molecule rather than the more commonly observed non-planar coordination, *e.g.* the tetrahedral coordination about the water molecule in the crystal structure reported for 5-hydroxybarbituric acid monohydrate (dialuric acid) by Alexander & Pitman (1956). In barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961) the water molecules were both shown to be in threefold planar coordination within the limits imposed by the experimental data.

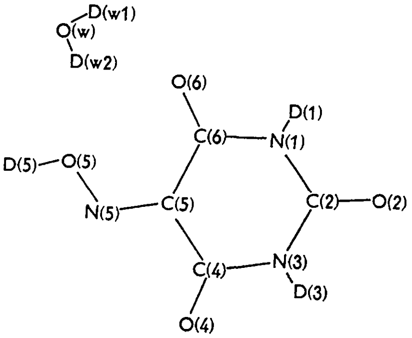

Fig. 1. Perdeuterated violuric acid monohydrate.

In violuric acid monohydrate (Craven & Mascarenhas, 1964) the water molecule has been shown by three-dimensional X-ray analysis to be apparently in fourfold planar coordination with two hydroxyimino oxygen atoms and two carbonyl oxygen atoms. There are six distances in the range 2·56 to 2·96 Å among these five atoms, but only three hydrogen atoms are available for the hydrogen bonding of each water molecule. A two-dimensional neutron diffraction analysis of the crystal structure of perdeuterated violuric acid monohydrate has been undertaken in order to determine the deuterium atom positions and hence the arrangement of hydrogen bonds.

Experimental

The structure analysis was carried out on perdeuterated rather than hydrogenated violuric acid monohydrate in order to avoid the excessive incoherent neutron scattering from the hydrogen atoms and to take advantage of the coherent scattering

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* Preceding paper.

amplitude for deuterium being positive and almost twice the magnitude of that for hydrogen. Deuterated crystals were obtained by evaporation in a desiccator of a solution of dehydrated violuric acid in 98% heavy water. Two successive crystallizations were carried out, the first over a period of several weeks and the second overnight. For the neutron diffraction work, larger crystals were readily grown from a supersaturated solution with seeds from the second batch of crystals. The crystals were pale orange with orthorhombic pyramidal habit, showing the principal forms {111} and {011}. The cleavage plane (100) was frequently also a twinning plane.

The crystals are orthorhombic, space group $Cmc2_1$ with cell parameters

$$a = 6.217 \pm 0.002,\ b = 14.373 \pm 0.002,\ c = 7.516 \pm 0.001\ \text{Å}$$

with four molecules per cell. The observed crystal density is 1.782 ± 0.005 g.cm^{-3}. Experimental details concerning these data have been previously reported (Craven & Mascarhenas, 1964).

The neutron intensity data were measured at the Westinghouse Testing Reactor, Waltz Mills, Pennsylvania with apparatus described by Takei, Stewart & Shirane (1960). A neutron wavelength of 1·14 Å was obtained by means of a Cu(111) monochromator. The estimated flux at the spectrometer axis was 3×10^7 thermal neutrons.min^{-1}cm^{-2}. The spectrometer was coupled in the $\theta - 2\theta$ mode to the detector and operated by step scanning at intervals of 0·1° in 2θ. The detector was a high pressure BF_3 proportional counter used in conjunction with another counter monitoring the direct beam.

With a crystal of dimensions approximately $1.3 \times 0.5 \times 0.5$ mm^3, *a* being parallel to the greatest length of the crystal, only the strongest 0*kl* reflexions could be readily detected. The crystal finally selected for data collection was cut from a cleavage plate 2·8 mm thick and was of approximately square cross section with an edge of 3·2 mm.

The 67 reflexions 0*kl* which were examined included all reflexions in the zone for which $2\theta < 80°$ and corresponded closely to the number of reflexions accessible to Cu $K\alpha$ X-radiation. Of these intensities, only two were too weak to be recorded. No corrections were applied for neutron absorption.

The structure determination

As in the case of the X-ray structure analysis, the structure determination was carried out in two parts, firstly, assuming the C, N and O parameters derived from the X-ray photographic intensity data and later assuming the revised parameters derived from the more accurate X-ray counter intensity data.

A consideration of the crystal structure of perdeuterated violuric acid monohydrate as determined by X-ray analysis led to the proposal of the hydrogen bonding schemes (I) and (II) shown in Fig. 2 as being the most probable. These models were tested by calculating the neutron structure factors 0*kl* using the first set of atomic parameters from the X-ray analysis for carbon, nitrogen and oxygen atoms (including the anisotropic thermal parameters) and the postulated parameters for the deuterium atoms, the latter all being assumed to have an isotropic thermal parameter of $B = 5.0$ Å^2. The scattering lengths used were $b_C = 0.66$, $b_O = 0.58$, $b_N = 0.94$ and $b_D = 0.65$ Fermi units (Schull & Wollan, 1951). The *R* indices according to the usual definition were 0·19 for model (I), 0·34 for model (II) and 0·34 for a calculation in which the deuterium atoms were omitted. The scale factors in each of these calculations were adjusted individually.

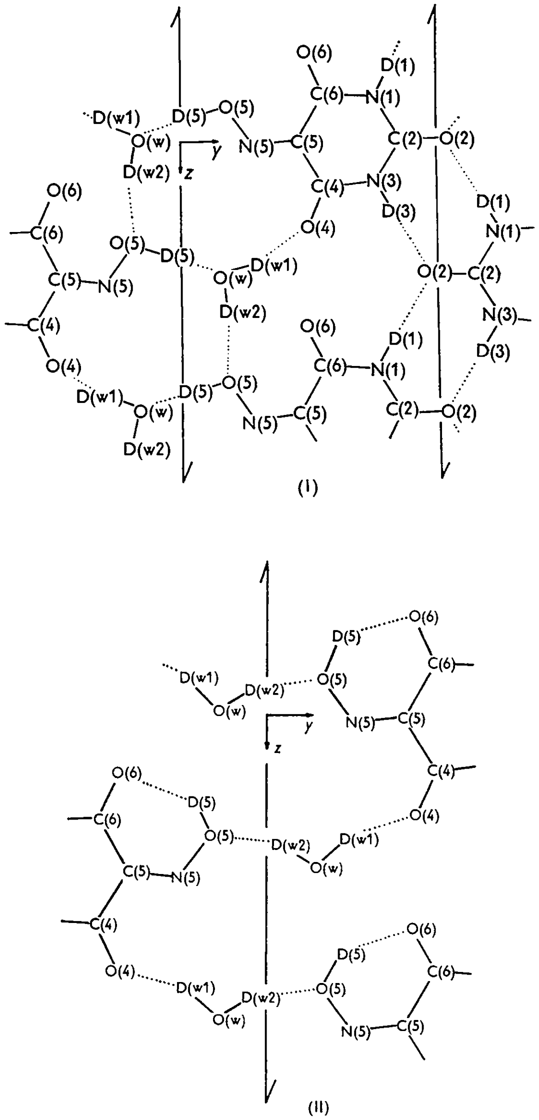

Fig. 2. The initially proposed structures for perdeuterated violuric acid monohydrate.

A difference Fourier synthesis of neutron scattering density was calculated on the basis of model (I) in which the assumed contribution from the carbon, nitrogen and oxygen atoms was removed. This projection completely resolved the deuterium atom peaks and showed no evidence of disorder of these atoms with respect to alternative positions. It was apparent that the initially assumed position of the water molecule was not quite correct and that the water molecule should be rotated in order to make the D(w2) atom approximately equidistant from neighboring O(5) and O(6) atoms.

The revised model was subjected to three cycles of difference Fourier and structure factor calculations allowing the individual isotropic temperature factors and positional parameters for the deuterium atoms to vary. FORTRAN programs for the IBM 7070 computer were written for these calculations (Craven, unpublished). At this stage there were no further significant parameter changes and the R index was 0·15.

The parameter refinement was concluded by two cycles of least squares assuming the revised values of the parameters for the carbon, nitrogen and oxygen atoms derived from the completed X-ray structure analysis. This was done on an IBM 704 computer with the Busing & Levy full matrix program (1959) in order to minimize the function

$$R=\Sigma w(|F_o|-|F_c|)^2.$$

Individual reflexions were weighted according to the e.s.d. in observed structure amplitudes which were assumed to be given by

$$\sigma(F)=\sigma(N)+0\cdot05|F|$$

where $\sigma(N)$ was the estimated error in structure amplitude derived from the counting statistics and the uncertainty in background level.

Although there were no large changes in the structure as a result of the least-squares refinement, the agreement between observed and calculated structures was much improved, giving a final R index of 0·076 and a weighted R index of 0·100. The observed and calculated structure factors are listed in Table 1. There is some evidence of systematic error in the larger observed structure amplitudes attributable to extinction effects, but this was not taken into account in the structure analysis. The final values of the structure parameters with their e.s.d.'s are listed in

Table 1. *The observed and calculated structure factors, 0kl*

k	l	$10\|F_o\|$	$10\|F_c\|$	$10A_c$	$10B_c$
0	2	42	40	31	−26
	4	27	32	23	−22
	6	129	134	124	51
	8	31	31	31	6
	2	17	11	−11	0
	1	58	60	14	−59
	2	69	70	68	−16
	3	72	77	−12	77
	4	48	54	43	−33
	5	35	33	−33	6
	6	81	82	−70	−42
	7	89	89	−35	−82
	8	71	67	65	16
	9	62	47	−13	45
4	0	62	65	−65	0
	1	34	37	29	−23
	2	15	17	0	−17
	3	102	112	48	−102
	4	60	60	59	−6
	5	22	19	11	−16
	6	48	47	46	−9
	7	58	60	−15	−59
	8	58	61	−53	−31
6	0	130	150	−150	0
	1	51	51	22	47
	2	64	67	67	−2
	3	30	29	18	−23
	4	22	24	−24	0
	5	61	62	41	−46
	6	50	44	−40	−19
	7	36	34	10	32
	8	38	33	−28	18
8	0	122	134	134	0
	1	83	86	−36	75
	2	6	5	−2	−5
	3	16	18	−18	3
	4	67	68	−68	2
	5	43	38	9	37
	6	71	67	62	25
	7	47	42	22	36
	8	35	34	−34	−4
10	0	26	29	29	0
	1	24	22	−10	19
	2	26	28	−25	12
	3	179	203	−19	202
	4	46	39	−19	−33
	5	43	38	−2	38
	6	29	28	−18	−22
12	0	10	16	16	0
	1	27	28	28	12
	2	14	16	12	−10
	3	67	70	68	−15
	4	99	100	100	6
	5	24	21	6	20
	6	35	32	−32	1
14	0	63	59	59	0
	1	89	78	24	74
	2	59	52	51	−14
	3	42	36	22	−29
	4	68	64	62	14
	5	39	49	2	5
16	0	3	3	3	0
	1	18	15	−7	13
	2	3	3	−1	−3
	3	40	40	−14	−37
	4	24	26	−24	9
18	0	49	45	−45	0

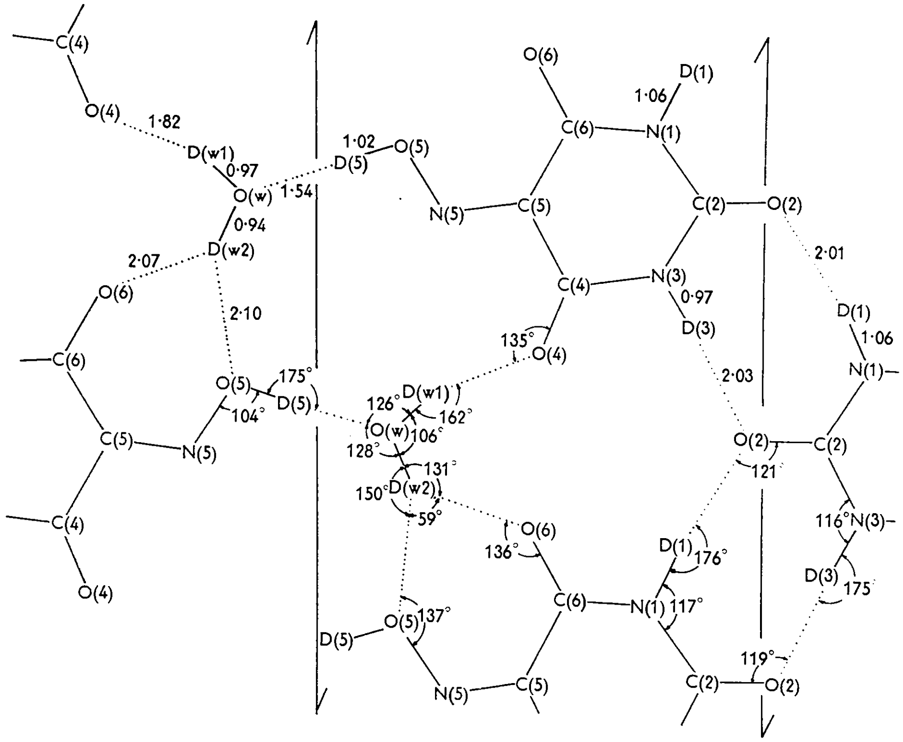

Fig. 3. The interatomic distances and angles involving deuterium atoms.

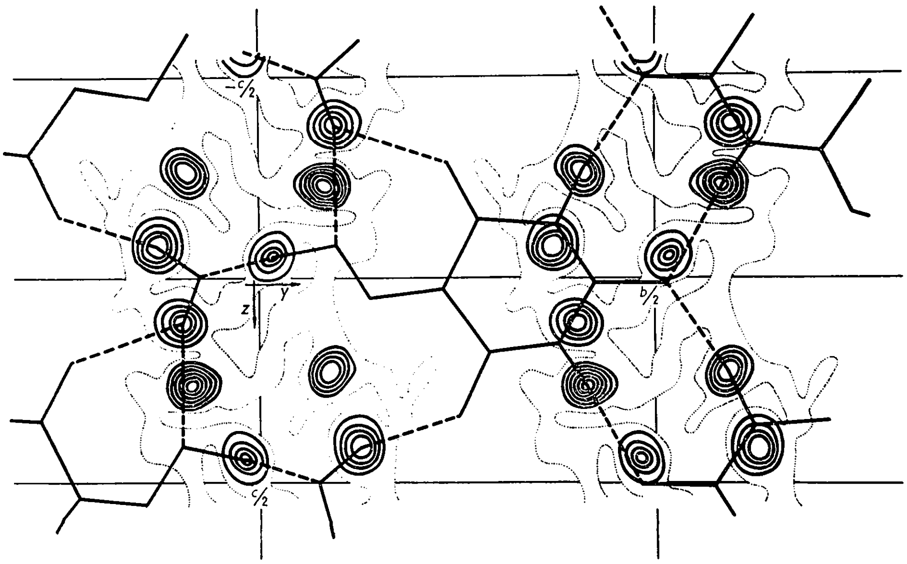

Fig. 4. The final Fourier synthesis of neutron scattering density from which the assumed scattering density of the carbon, nitrogen and oxygen atoms has been subtracted. The contours are at intervals of 0·5 Fermi unit.Å^{-2} with the zero contour shown dotted.

Table 2 and the resulting interatomic distances and angles involving deuterium atoms are shown in Fig. 3. There has been no attempt to correct these bond lengths for the effect of molecular oscillations. The e.s.d. in a bond length involving a deuterium atom is 0·025 Å. The e.s.d. in an angle subtended at a deuterium atom is 2·0°. The e.s.d. in other angles involving deuterium atoms is 1·4°.

In Fig. 4 is shown the final Fourier synthesis of neutron scattering density from which the assumed contribution from the carbon, nitrogen and oxygen atoms has been subtracted.

Table 2. *Atomic parameters and their e.s.d.'s*

(*a*) Parameters determined from neutron data

Atom	*y*/*b*	σ(*y*/*b*)	*z*/*c*	σ(*z*/*c*)	*B* (Å^2)	σ(*B*)
D(1)	0·4112	0·0013	−0·274	0·0029	2·26	0·39
D(3)	0·4179	0·0010	0·266	0·0024	1·46	0·37
D(5)	0·0224	0·0013	−0·063	0·0032	3·05	0·59
D(w1)	0·1327	0·0012	0·413	0·0033	3·30	0·49
D(w2)	0·1063	0·0010	0·610	0·0032	2·79	0·41

(*b*) Parameters determined from X-ray data (Craven & Mascarenhas, 1964)

Atom	*y*/*b*	*z*/*c*	B_{22} (Å^2)	B_{33} (Å^2)	B_{23} (Å^2)
C(2)	0·4282	0	1·42	1·69	−0·10
C(4)	0·2847	0·1774	1·62	2·16	−0·07
C(5)	0·2302	0·0121	1·49	1·40	0·39
C(6)	0·2803	−0·1639	1·72	1·30	−0·13
N(1)	0·3755	−0·1506	1·32	1·43	0·19
N(3)	0·3801	0·1588	1·61	1·37	0·21
N(5)	0·1422	0·0333	2·07	3·57	0·12
O(2)	0·5134	0·0008	1·42	1·95	0·05
O(4)	0·2508	0·3251	1·88	1·24	0·27
O(5)	0·0890	−0·1112	1·64	2·00	−0·18
O(6)	0·2432	−0·3034	2·01	1·10	−0·56
O(w)	0·0805	0·4945	1·05	2·92	−0·37

Discussion

The bonds O(5)–D(5) and C(5)–N(5) are almost parallel so that there is no intramolecular hydrogen bond O(5)–D(5) · · · O(6) in this crystal structure.

The observed bond lengths N(1)D(1) (1·06 Å) and N(3)D(3) (0·97 Å) involving trigonally hybridized nitrogen are believed to be the first to be determined by neutron diffraction methods. The e.s.d. in the difference between these bond lengths is 0·35 Å so that the bond N(1)D(1) may be said to be significantly longer than the bond N(3)D(3). This difference would not be expected from a consideration of the similarity in the four C–N bond lengths of the pyrimidine ring, as determined in the X-ray analysis and from the fact that both atoms D(1) and D(3) participate in weak N–D · · · O hydrogen bonds. These N–D bond lengths may be compared with the average N–H lengths observed in the crystal structure of urea, which are 0·99 ± 0·02 Å as determined by neutron diffraction (Worsham, Levy & Peterson, 1957) and 1·04 ± 0·01 Å as determined by proton magnetic resonance methods (Andrew & Hyndman, 1953; Kromhout & Moulton, 1955).

The distances N(1)···O(2) (3·07 Å) and N(3)···O(2) (3·00 Å) are longer than is commonly reported for N · · · O hydrogen bonding distances, although comparable for example, to the N–H · · · O distance of 3·07 Å in 4-nitroaniline (Trueblood, Goldish & Donohue, 1961). The nature of the molecular packing apparently accounts for the weakness of these N–D · · · O(2) interactions since although compression of the structure along the *z* direction would decrease the N · · · O(2) distance and strengthen these interactions, this would be at the expense of increased repulsion between atoms O(4) and O(6), already quite close to each other (2·79 Å) for a van der Waals interaction. Compression of the structure along the *y* direction would be at the expense of further bending of the angles N(1)D(1)O(2) (176°) and N(3)D(3)O(2) (175°), thus weakening the hydrogen bonds.

The observed value of the isotropic thermal parameter for atom D(1) (2·26 Å) is possibly significantly greater than that of D(3) (1·46 Å). Also the difference Fourier map (Fig. 4) indicates considerable anisotropic thermal motion of atom D(1) with maximum amplitude normal to the N(1)D(1) bond, whereas the anisotropy is much less for atom D(3). This difference in behaviour may be correlated with the stronger interaction N(3)–D(3) · · · O(2).

The observed O–D bond lengths in the D_2O molecule (0·97 and 0·94 Å) are not significantly different, but are shorter than the O–D bond lengths (1·01 Å) in deuterated ice (Peterson & Levy, 1957) as determined by neutron diffraction methods.

The present results have not been corrected for the shortening effect of libration of the D_2O molecule which could be as much as 0·04 Å. The observed bond angle DOD (106°) does not differ significantly from either of the values (104½°, 109½°) derived from alternative descriptions of the structure of deuterated ice by Chidambaram (1961) and Peterson & Levy (1957).

The oxygen atom of the D_2O molecule is acceptor for a short (2·56 Å) hydrogen bond O(5)–D(5)···O(w) from the hydroxyimino group in which the D(5) atom is close to the line of centers O(5) · · · O(w). (The angle O(5)D(5)O(w) is 175°.) The O(5)–D(5) bond length (1·02 Å) is shorter than might be expected from the empirical O · · · O distance *versus* O–H distance curve of Atoji & Rundle (1958) and clearly, this hydrogen bond is not of the symmetrical type as observed for the somewhat shorter hydrogen bond (2·54 Å) in the crystal structure of potassium hydrogen bisphenylacetate (Bacon & Curry, 1957).

The hydrogen bond O(w)–D(w1) · · · O(4) between the water molecule and a carbonyl oxygen atom is of length 2·76 Å, which is close to the O···O distance (2·75 Å) in deuterated ice. However, the hydrogen bond O(w)–D(w) · · · O(4) is much more severely bent than in the bent hydrogen bond model for deuterated ice proposed by Chidambaram (1961) as can be seen from the respective ODO angles of 162° and 176°.

The deuterium atom D(w2) interacts with both the O(5) and O(6) atoms of a neighbouring violuric acid molecule, forming what may be called a 'bifurcated hydrogen bond'. Thus the D(w2) · · · O(5) and D(w2) · ·· O(6) distances are similar (2·07 and 2·10 Å) and although the bond O(w)–D(w2) makes a smaller angle (21°) with the line of centers O(w) · · · O(5) than with the line of centers O(w) · · · O(6) (34°), it may be said that the atoms O(5) and O(6) participate to about the same extent in the interaction.

Although bifurcated hydrogen bonds have been reported in a number of other crystal structures, these have usually been disputed. The only well authenticated example of a bifurcated hydrogen bond is in the crystal structure of glycine, which has been studied by X-ray diffraction methods (Albrecht & Corey, 1939; Marsh, 1958) and by neutron diffraction methods (Burns & Levy, 1958). In this bifurcated hydrogen bond, one of the two acceptor oxygen atoms participates much more effectively than the other.

For an isolated system consisting of a donor atom a hydrogen atom and an acceptor atom, a colinear configuration is expected to have minimum energy. In crystal structures which feature hydrogen bonds, the requirements of molecular stereochemistry may conflict with the requirement of linear hydrogen bonding so that the observed molecular packing and hydrogen bond configuration must be regarded as a compromise. The influence of stereochemistry may be considerable, particularly in the case of a structure such as violuric acid monohydrate, in which the majority of atoms are potential acceptor or donor atoms in hydrogen bonds. The structure (I) was initially proposed for perdeuterated violuric acid monohydrate because although the angle O(4)O(w)O(5) is about 10° larger than the angle DO(w)D this structure possessed the water molecule orientation which best satisfied the linear hydrogen bond criterion. However, in the observed structure, the water molecule was found to be rotated by about 16° from the orientation postulated in (I). Thus, all the nearest neighbour atoms, the three acceptor atoms O(4), O(5) and O(6), together with the donor group O(5)D(5) must influence the orientation of the water molecule.

More detailed stereochemical considerations suggest reasons for the observed bifurcated configuration having a lower energy than configuration (I). In the observed configuration the interaction O(w)–D(w2). O(6) would certainly be stronger than in (I). This would probably be the case for the interactions O(w)–D(wl) · · · O(4) and O(w)–D(wl) · · · O(4) also, because the deuterium atoms would be closer to a lone pair of electrons belonging to the trigonally hybridized acceptor oxygen atoms. The interaction O(5)–D(5) · · · O(w) would also be stronger in the observed configuration since the atom D(5) would be in a more symmetrical position with respect to the lone pair of electrons on atom O(w), which is presumably tetrahedrally hybridized. (The observed angles D(5)O(w)D(wl) and D(5)O(w)D(w2) are 126° and 128°.)

The crystal structure of perdeuterated violuric acid monohydrate might consist either of coplanar sheets of atoms undergoing considerable thermal vibrations normal to the sheets, or of a structure disordered by small displacements of the atoms from coplanarity and with a compensating reduction in atomic thermal vibrations. In a nonplanar structure, one half of the hydrogen bonding interactions O(5)–D(5) · · · O(w), for example, would be strengthened by being directed preferentially toward one of the lone pairs of electrons in the tetrahedral orbitals of the water oxygen atom, O(w). However, the remaining interactions O(5)–D(5) · · · O(w) would necessarily be weakened. Neither the X-ray nor the neutron data used in the analyses permit a distinction between the alternative structures.

The complete substitution of hydrogen by deuterium atoms in the structure of violuric acid monohydrate results in an expansion of the unit cell by 0·014 Å and 0·008 Å along the *b* and *c* directions respectively and in a contraction of 0·007 Å along the *a* direction. These expansions are highly significant but the contraction only possibly significant in terms of the e.s.d. of 0·003 Å in Δa and Δb and 0·0025 Å in Δc. The greater expansion along *b* is consistent with the isotope effect which is usually observed in hydrogen bonded crystal structures (Robertson & Ubbelohde, 1939; Nordman & Lipscomb, 1951) since the *b* direction corresponds approximately to the orientation of the only short hydrogen bond (O(5)–D(5) · · · O(w) 2·56 Å) in the crystal structure.

This work was supported in part by a grant (NB-2763) from the U.S. Public Health Service, National Institutes of Health and by The Westinghouse Research Laboratories, Pittsburgh, Pa.

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