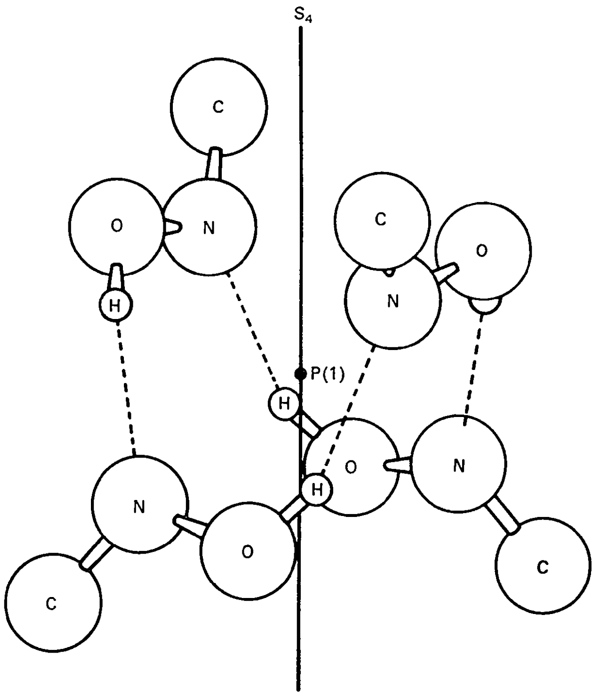

Fig. 3. Tetrameric hydrogen bond network of *anti*-α-bromoacetophenone oxime. The point $P(1)$ has coordinates ($\frac{1}{2}$,0,$\frac{1}{4}$) and is the invariant point of the S_4 operation. The nitrogens and oxygens occupy nearly tetrahedral positions.

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Perdeuterated Biuret Hydrate $C_2D_5N_3O_2.(0{\cdot}77D_2O)$

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Biuret hydrate $C_2D_5N_3O_2.nD_2O$; monoclinic, space group $P2_1/c$ (except for the water molecules); $a=3{\cdot}6518$ (6), $b=17{\cdot}767$ (5), $c=9{\cdot}048$ (1) Å, $\beta=118{\cdot}91$ (1)°; $d_{\text{meas}}=1{\cdot}596$ (1) g cm^{-3} at 25°C, corresponding to $Z=4$, $n=0{\cdot}769$ (4). The crystal structure as determined from X-ray (Cu $K\alpha$) diffractometer data is the same as for the hydrogenated material, except in detail. Full-matrix least-squares refinement gave $n=0{\cdot}769$ (15), and e.s.d.'s of 0·003 Å in C–N, C–O bond lengths, 0·05 Å in N–D bond lengths and 0·2° in bond angles at nitrogen and carbon atoms. The water molecules appear to be disordered, forming zigzag hydrogen bonds of finite length, as in the hydrates of caffeine and thymine.

Experimental

Biuret was prepared by gently heating urea (Werner, 1923) and purified by several crystallizations from water and finally ethanol. Anhydrous biuret (8g) was then distilled almost to dryness three times with 50 ml of 99·5 mol.% heavy water, supplied by the U. S. Atomic Energy Commission. Final crystallization of deuterated biuret hydrate was by slow evaporation of a heavy-water solution at room temperature in an atmosphere of nitrogen. Crystal-density measurements were made on several large, clear crystals using the method of flotation in a mixture of carbon tetrachloride and dibromoethane. A long needle was cleaved parallel to (100) to give a crystal of dimensions 0·30, 0·15, 0·30 mm along **a***, **b** and **c**. The crystal was immediately

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* $R=(\sum_h|\Delta F|/\sum_h|F_{\text{meas}}|)$.

coated with lacquer ('Crystal Clear,' No. 1302, Krylon Inc., Norristown, Pa.), in order to prevent loss of crystal water and hydrogen exchange with atmospheric moisture.

The X-ray data were measured on a four-circle automatic diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), with the crystal mounted with **a*** along the φ-axis. Lattice parameters were determined from measurements on reflections 100, 0180, 008 using the method of Bond (1960). Integrated intensities were measured from θ–2θ scans at 2°/min with 20 sec background measurements at both scan limits. Of 844 nonsymmetry related reflections with $\sin\theta/\lambda \leq 0{\cdot}58$ Å^{-1}, 61 were found to have integrated intensities $I < \sigma(I)$. They were considered to be unobservably weak and were assigned values of $I = \sigma(I)/2$.

Atomic parameters (Table 1) were refined by full-matrix least-squares methods, starting from the values of Hughes, Yakel & Freeman (1961) for biuret hydrate. The function minimized was $\sum_{h}(\varDelta F)^2/\sigma^2(F)$, where $\varDelta F = |F_{\text{meas}}| - |F_{\text{calc}}|$ and $\sigma^2(F) = 0{\cdot}09 + 0{\cdot}0276|F| + 0{\cdot}021|F|^2$. The atomic scattering factors were those taken from *International Tables for X-ray Crystallography* (1968), except deuterium, for which Stewart, Davidson & Simpson's (1965) values for hydrogen were assumed. The deuterium atoms were assigned the same anisotropic temperature factors as the atoms to which they are bonded. Water deuterium atoms were not located. The refinement converged at an R value* of 0·066, or 0·063 omitting unobservably weak reflections. The standard deviation in an observation of unit weight was 0·95. Reflections 011, 020, 100, 110 and 111 were omitted from the refinement because $|F_{\text{meas}}|$ was considerably less than $|F_{\text{calc}}|$. The table of $|F_{\text{meas}}|$ and $|F_{\text{calc}}|$ is available on request.†

The least-squares correlation matrix shows values in the range 0·45–0·65 for the correlations between x and z, β_{11} and β_{13}, β_{33} and β_{13} of the same atom. These are attributed to the nonorthogonality of the unit cell. Correlation parameters of 0·5 are also observed between the occupancy factor (n) and each of the thermal parameters β_{11}, β_{22}, and β_{33} of the water oxygen atom. These correlations did not affect the convergence of the least-squares refinement. The final bond lengths and angles and hydrogen bonding distances are shown in Fig. 1. The e.s.d.'s are 0·003 Å in C–N and C–O distances, 0·05 Å in N–D distances, 0·2° in N–C–N and N–C–O angles, and 3° in C–N–D angles.

The composition of the hydrate $C_2D_5N_3O_2.nD_2O$ as determined from the lattice parameters and crystal density is $n = 0{\cdot}769$ (4). This value was obtained by assuming 100% deuteration and taking Avogadro's number to be $6{\cdot}0225 \times 10^{23}$. This agrees well with the

Table 1. *Atomic parameters*

Positional parameters are given as fractional coordinates. Thermal parameters are given according to the expression $T = \exp(-\sum_i \sum_j \beta_{ij} h_i h_j)$. Principal values ($U_i$) for the r.m.s. amplitudes of thermal vibration are in Å. **The angle (φ) between U_3** and **a*** is given in degrees. The e.s.d.'s given in parentheses refer to the least significant digits of the parameter values.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	U_1	U_2	U_3	φ
C(1)	0·5859 (7)	0·26360 (14)	0·3565 (3)	0·084 (3)	0·00220 (8)	0·0111 (5)	0·0004 (3)	0·019 (1)	−0·0003 (1)	0·16	0·19	0·21	14
C(2)	0·5931 (7)	0·38502 (14)	0·4960 (3)	0·088 (3)	0·00214 (8)	0·0123 (5)	−0·0002 (3)	0·022 (1)	−0·0002 (1)	0·16	0·19	0·22	21
N(1)	0·5717 (8)	0·19023 (17)	0·3818 (3)	0·147 (3)	0·00189 (8)	0·0146 (5)	−0·0006 (3)	0·033 (1)	−0·0003 (1)	0·17	0·18	0·28	7
N(2)	0·6136 (7)	0·30736 (12)	0·4878 (3)	0·105 (3)	0·00198 (7)	0·0111 (4)	0·0003 (3)	0·023 (1)	−0·0002 (1)	0·15	0·18	0·23	8
N(3)	0·5507 (8)	0·42506 (14)	0·3658 (3)	0·145 (3)	0·00217 (8)	0·0141 (5)	0·0025 (4)	0·032 (1)	0·0007 (1)	0·17	0·18	0·28	12
O(1)	0·5784 (7)	0·29015 (10)	0·2296 (2)	0·145 (3)	0·00234 (7)	0·0120 (4)	−0·0003 (3)	0·031 (1)	0·0000 (1)	0·15	0·19	0·27	5
O(2)	0·6109 (6)	0·41209 (9)	0·6255 (2)	0·132 (3)	0·00201 (6)	0·0127 (4)	0·0011 (3)	0·027 (1)	−0·0004 (1)	0·16	0·19	0·26	5
O(W)	0·1988 (7)	0·04409 (25)	0·4600 (5)	0·281 (9)	0·00502 (19)	0·0234 (9)	−0·0017 (9)	0·017 (2)	0·0027 (3)	0·24	0·30	0·44	40
D(1)	0·59 (2)	0·176 (2)	0·482 (7)										
D(2)	0·55 (2)	0·164 (3)	0·307 (7)										
D(3)	0·64 (2)	0·281 (2)	0·580 (6)										
D(4)	0·52 (2)	0·408 (2)	0·265 (7)										
D(5)	0·54 (2)	0·477 (3)	0·373 (5)										

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† This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP. 30088. Copies may be obtained through the Executive Secretary. International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

water oxygen atom occupancy factor $n=0{\cdot}769$ (15) as determined from the least-squares refinement, suggesting that there was no significant change in crystal composition during the data collection.

The composition of the hydrogenated material $C_2H_5N_3O_2.nH_2O$ has been reported to be $n=0{\cdot}77$ (5) from lattice parameters and crystal density,* decreasing to $n=0{\cdot}6$ from a best fit of observed and calculated electron densities (Hughes, Yakel & Freeman, 1961). In a vapor pressure/composition study, Rollet & Cohen-Adad (1951) found that crystalline biuret hydrate contained 11·9 to 12·2 weight % of water, corresponding to $0{\cdot}773 < n < 0{\cdot}795$.

Discussion

The crystal structures of deuterated and hydrogenated biuret hydrate differ only in detail. Comparison of biuret bond lengths and angles (Fig. 1) is of limited value because of the much larger e.s.d.'s for the hydrogenated molecule (0·024 Å in C–N and C–O bond lengths; 1·6° in bond angles), but there are no differences greater than 2σ. Presently reported bond lengths and angles also agree well with the appropriate fragment of triuret (Carlström & Ringertz, 1965). Corresponding bond lengths in the two urea moieties of deuterated biuret are not significantly different if some allowance is made for the least-squares standard deviations being underestimated. The N, C and O atoms of each of these moieties are coplanar within 0·004 Å, with a dihedral angle between these planes of 6·3°. The torsion angle which shows the greatest departure from an idealized *syn* or *anti* configuration (7·5°) is about the central bond in C(2)–N(2)–C(1)–O(1). The puckering of the molecules of both biuret and triuret appears to result from repulsions across the pseudo-rings which arise from the formation of the intramolecular hydrogen bonds. It is of interest that the angles C(1)–N(2)–C(2) and N(2)–C(2)–N(1) are very similar to the internal ring angles C–N–C (126°) and N–C–N (116°) observed in the polymorphs of amobarbital (Craven & Vizzini, 1969). The barbiturate pyrimidine ring is puckered also, with torsion angles of about 6°.

Biuret molecules are hydrogen bonded in sheets (Fig. 1) which are stacked with a spacing of $d_{100}=3{\cdot}1965$ (5) Å. The water molecules are in zigzag chains parallel to **a** (Fig. 2), each chain being in a tunnel which passes through the hydrogen bonded biuret sheets. The water oxygen atom sites are fractionally occupied ($n=0{\cdot}77$) and correspond to relatively diffuse peaks in the electron density distribution (Fig. 2). The least-squares

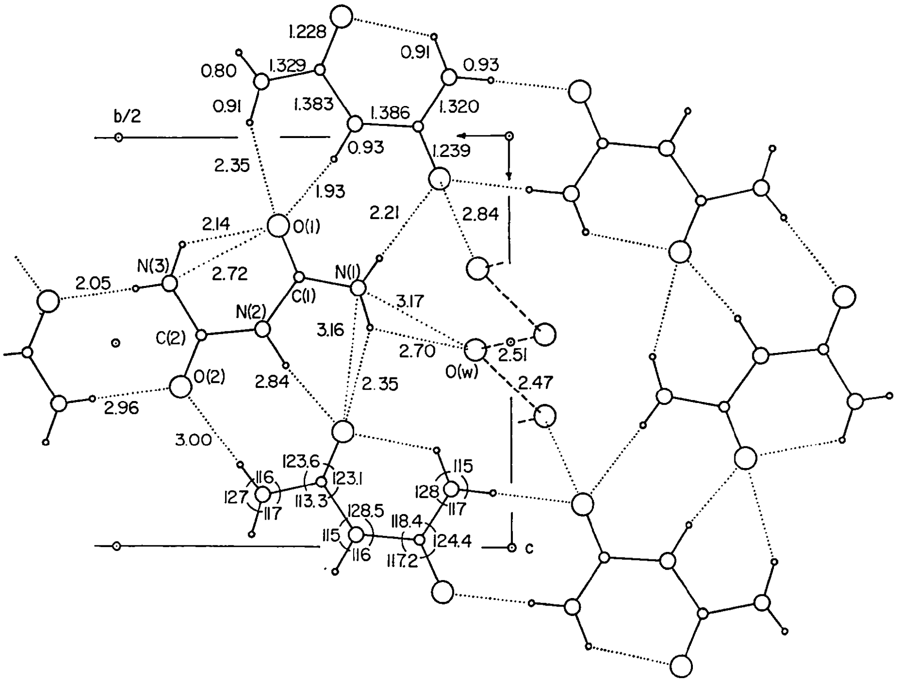

Fig. 1. The crystal structure of deuterated biuret hydrate in projection down **a***. Biuret molecules are shown for the hydrogen bonded sheet which is near $x=\frac{1}{2}$. A zigzag chain of water molecules parallel to **a** is shown passing through this sheet. Bond distances are in Å and bond angles in degrees.

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* Crystals of $C_2H_5N_3O_2.nH_2O$ from a different sample were found to give $a=3{\cdot}638$ (4), $b=17{\cdot}75$ (2), $c=9{\cdot}027$ (10) Å, $\beta=118{\cdot}78$ (7)°; $d_{\text{meas}}=1{\cdot}512$ (1) g cm^{-3}, $n=0{\cdot}735$ (12) (Craven, Freeman & Sabine, unpublished). The values for c and d_{meas} are significantly different ($9{\cdot}18\pm0{\cdot}01$ Å and $1{\cdot}520\pm0{\cdot}004$ g cm^{-3}) from those of Hughes, Yakel & Freeman (1961). These variations in crystal data may be real and due to differences in composition and rate of loss of water.

refinement gave a maximum apparent r.m.s. amplitude of thermal vibration of 0·44 Å (Table 1). Other notable features of the water molecule arrangement are the centroid to centroid distances O(W)$\cdots$O(W) which are shorter (2·47 Å and 2·51 Å with e.s.d.'s of 0·007 Å) than is usual in O–H$\cdots$O hydrogen bonds.

The crystalline hydrates of caffeine (Sutor, 1958) and thymine (Gerdil, 1961) have very similar arrangements of water molecules. Gerdil & Marsh (1960), Gerdil (1961) and Hughes, Yakel & Freeman (1961) have suggested that the diffuse water oxygen peaks represent disorder as well as the expected thermal vibration. If the O$\cdots$O distance is actually about 2·70 Å, then a hydrogen-bonded chain of water molecules would have a longer repeat distance than the surrounding structure. The chains would be interrupted by a vacancy after seven or eight water molecules, because of unfavorable interactions which would arise between water and surrounding molecules. In the case of biuret hydrate, progression along the chain would lead to increasingly longer O(W)–D$\cdots$O(2) distances (O$\cdots$O centroid to centroid, 2·84 Å; Fig. 2) and shorter non-bonded O(W)$\cdots$N(1) distances (centroid to centroid 3·17 Å; Fig. 2). This model satisfactorily accounts for the crystal structure of $C_2D_5N_2O_3.0{\cdot}77D_2O$ as determined from X-ray diffraction data. A refinement of this model, including the arrangement of the water deuterium atoms, must await a neutron diffraction study. However, no further work of this kind is in progress.

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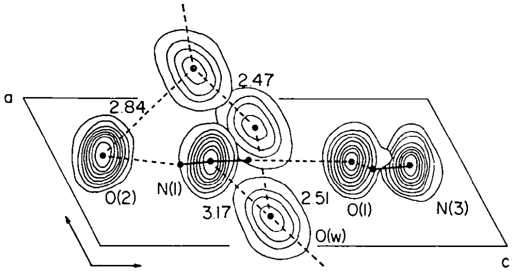

Fig. 2. The electron density in deuterated biuret hydrate in the region of $y=0$. Contours are at intervals of 1 e Å^{-3}, beginning at 1 e Å^{-3}. A zigzag chain of water molecules is shown together with atoms from the sheet of biuret molecules which form half of a hydrogen bonded ring surrounding the water chain. Atoms O(2), N(1) and the intramolecularly hydrogen bonded O(1)$\cdots$DN(3) are from three different biuret molecules. The shortest distances between biuret and water oxygen atoms are in Å.

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