

explains the tight packing of the structure that presents rather unusual short intermolecular contacts.

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References

- ALBANO, V., DOMENICANO, A. & VACIAGO, A. (1966). *Gazz. chim. Ital.* **96**, 922.
 BARRETT, A. N. & PALMER, R. A. (1969). *Acta Cryst.* **B25**, 688.

- GIORDANO, F. & RIPAMONTI, A. (1967). *Acta Cryst.* **22**, 678.
 HANIC, F. (1966). *Acta Cryst.* **21**, 332.
 HEYL, D., LUZ, E., HARRIS, S. A. & FOLKERS, K. (1951). *J. Amer. Chem. Soc.* **73**, 3430.
 KARLE, I. L. & BRITTS, K. (1966). *Acta Cryst.* **20**, 118.
 KARLE, J. & KARLE, I. L. (1965). *Computing Methods in Crystallography*, p. 151. Oxford: Pergamon Press.
 NATTA, G., CORRADINI, P. & BASSI, I. W. (1961). *J. Polymer Sci.* **51**, 505.
 PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746.
 UMBREIT, W. W. & GUNSALUS, I. C. (1949). *J. Biol. Chem.* **179**, 279.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1971). **B27**, 134

Electron Density Distribution in Cyanuric Acid. I. An X-ray Diffraction Study at Low Temperature

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Cyanuric acid crystallizes in the monoclinic space group $C2/n$. The crystal structure was refined at both room and low temperature. The following data refer to the low-temperature work. The cell dimensions are $a = 7.749$ (1), $b = 6.736$ (3), $c = 11.912$ (4) Å, $\beta = 130.69$ (2)° (e.s.d. in parentheses). The 965 independent reflexions with $\sin \theta/\lambda < 0.8$ Å⁻¹ were measured carefully at 100°K with a non-automated diffractometer. Mo radiation with balanced Zr and Y filters and the ω -scan technique were used. Details of the apparatus are given. The structure was refined by anisotropic least-squares techniques, converging to $R = 0.038$. Average values for bond lengths and angles are: C-N = 1.372 (1), C-O = 1.220 (2) Å, N-C-N = 115.3 (1), C-N-C = 124.7 (1)°. Two types of N-H...O hydrogen bonds with lengths of 2.778 (3) and 2.798 (3) Å link the molecules together in layers nearly parallel to the plane $x = 0.25$. The residual density map shows maxima at the middles of the bonds and negative regions on either side of a bond. Lone pairs at angles of 120° to the C-O bonds are found at the oxygen atoms. There is no hole in the middle of the six-membered ring. Average values (in e.Å⁻³) for the maxima on the bonds are 0.40 for C-N, 0.24 for C-O and 0.25 for N-H. The maxima are extended in the π direction. It appears that the maxima and minima due to bonding effects become less pronounced if only reflexions within the copper sphere ($\sin \theta/\lambda < 0.6$ Å⁻¹) are considered. Thermal analysis according to Cruickshank showed that cyanuric acid cannot be regarded as a rigid body. A least-squares refinement with aspherical scattering factors for atoms in the valence state gave a poorer agreement between F_o and F_c ($R = 0.055$) than the refinement with spherical scattering factors for atoms in the ground state.

Introduction

During the formation of chemical bonds there is a change in the electron distribution of the participating atoms. Attempts have been made by Smith & Richardson (1965, 1967) to give a picture of these changes by quantum-mechanical calculations for some diatomic molecules consisting of first-row atoms. Even for these simple cases, the work showed that the calculated

changes depend very much on the assumptions made for the wave functions of the molecules. This clearly shows the need for direct experimental information. In principle this information can be obtained by X-ray diffraction as by this method the one-electron density function in a molecule can be determined. The study of cyanuric acid described in this paper was undertaken seven years ago to determine with what accuracy the electron density distribution in a molecule could be obtained. The work was carried out at low temperature in order to observe high order as well as low order reflexions and so to improve the resolution of the electron density maps. Moreover in this way errors due to thermal diffuse scattering, for which no corrections could be applied, were considerably reduced. A preliminary re-

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Apparatus for the low temperature study

Diffractometer

The intensities were measured on a non-automated three-circle diffractometer, analogous to that described by Furnas & Harker (1955) and to that commercially made available by Enraf-Nonius, Delft, Netherlands. During the construction of the diffractometer use was made of information kindly sent to us by Dr Furnas. The ranges available for φ , χ and θ (permanently coupled with the counter displacement 2θ) are 0–360°, 0–90° and 0–75° respectively. The φ – χ assembly could rotate over an ω -range of 12° with respect to θ . The crystal was at 215 mm from the focal spot and at 58 mm from the receiving slit. The dimensions of the collimator were such that all points within a sphere of 1 mm diameter around the centre of the apparatus could see a focal spot of 1 × 1 mm².

Incident X-ray beam

To keep errors due to dispersion effects small and to make it possible to observe high-order reflexions, it is desirable to use short wavelength radiation. We used molybdenum radiation obtained from a fine-focus Philips tube which could be rotated around a horizontal axis to change the take-off angle (at a take-off angle of 3° the effective focal dimensions are 0.4 × 0.4 mm²). The output of the tube in combination with a Philips generator PW 1010 appeared to be stable after a warm-up period of one hour. Both the long-period and the fast fluctuations appeared to be some 0.1 per cent. The homogeneity of the primary beam at the position of the crystal was checked by using a lead plate 0.5 mm thick having a small hole of diameter 0.03 mm, or by using a small crystal. It appeared that at a take-off angle of 3° the intensity of the Mo *K* radiation changed in the vertical direction by 4.5 per cent over a distance of 1 mm, due to the variation in the angle of view. At a take-off angle of 6° the beam appeared to be homogeneous (± 0.5 per cent) over a distance of 0.8 mm in both directions. Moreover the total intensity at a take-off angle of 6° is 1.5 times larger than at a take-off angle of 3°. We therefore decided to measure the intensities at a take-off angle of 6°. A larger take-off angle would have been advantageous for the homogeneity and the total intensity but would have required a wider collimator and increased the divergence of the beam.

Detection system

For the detection of the X-rays a scintillation counter with a NaI(Tl) crystal was used in conjunction with a single-channel pulse-height analyser. After about three hours the fluctuations of the detection system were negligibly small in comparison with the fluctuations in the incident beam. As the resolving time of the detection system was about 5.5 μ sec, attenuation foils were used to keep errors due to non-linearity smaller than one per cent. We used Zr-foil of 0.07 mm, which absorbed nearly 50 per cent of the Mo *K* α radiation. By using

from 0 through 9 foils attenuation factors between 1 and 357 could be obtained. To determine the attenuation factors within a standard deviation of 0.2 per cent the dead-time correction had to be accurately determined. This was done using the principle of the method of Trott (1960). The apparent absorption factor A' of a foil for Mo *K* α radiation is determined for a range of intensities I' , I' being the intensity (in counts per sec) measured without using this foil. It can be shown (Verschoor, 1967) that A' and I' obey the equation

$$A'(I') = A - I'\tau(A - 1)$$

where A is the true absorption factor and τ is the dead time. $A'(I')$ against I' gives a straight line from which both A and τ can be obtained. In our case the measured intensities did not obey the simple equation quoted above, however, and second order terms in I' were added to describe the relationship between A' and A . The deviations were caused by the pulse-height distribution shifting out of the discriminator window for high intensities due to piling up of the pulses.

Balanced filters

Errors in the intensity due to white radiation were kept small by applying the balanced-filter technique. This technique was preferred to the use of a monochromator crystal (LiF) as it appeared to give better homogeneity of the incident beam. Zr and Y were used as balanced filters. The Zr filter was of thickness of 3.6×10^{-3} cm. According to Soules, Gordon & Shaw (1956) the maximum intensity difference ΔI is obtained for a Zr filter of thickness 3.25×10^{-3} cm, whereas the relative standard deviation $\sigma(\Delta I)/\Delta I$ is minimal for thicknesses varying between 4.5 and 6×10^{-3} cm, depending on the wavelength distribution of the incident radiation. Yttrium was used in the form of a suspension of Y₂O₃ in a polymerized mixture of 90 per cent butyl methacrylate and 10 per cent methyl methacrylate. A polymethacrylate slice of the same thickness as the Y suspension was added to the Zr filter. By adjusting the angle between the plane of the Y filter and the incident beam a very good balance could be obtained if pulse-height discrimination was applied.

Low-temperature equipment

The cooling system shown in Fig. 2 is analogous to that described by Post, Schwartz & Fankuchen (1951). The crystal (f) was cooled by a flow of cold nitrogen gas surrounded by a jacket of room temperature dry nitrogen gas both obtained from an evaporation vessel containing liquid nitrogen. To lessen disturbances of the gas flow, which is necessary to avoid condensation of H₂O and CO₂, the outer tube was extended with a thin Mylar foil with negligible X-ray absorption characteristics. Moreover as it appeared that the part of the crystal holder in the gas streams should be as small as possible, the crystal was mounted in a short glass capillary fused on a thin glass fiber. The temperature of the crystal depended on the distance of the crystal

from the opening of the Dewar tube and on the flow-rate of the cooling gas. Thermocouple measurements indicated that, under favourable circumstances, a temperature of 83°K could be obtained. Perpendicular to the gas flow the temperature varied less than one degree over an area of 7 mm².

Experimental

Preparation of the crystals

Cyanuric acid containing less than one per cent impurity was commercially available (Fluka). Crystals were obtained by slow sublimation in a Pyrex tube (temperature 150 to 180°C, pressure less than 10⁻⁴ mm Hg), the time required for the sublimation being 1 to 4 months. In most cases the crystals were twinned on the (100) planes and had to be cleaved along this plane in order to get single specimens. Most crystals appeared to show a large mosaic spread, but after several attempts some crystals with a mosaic spread smaller than 2° were isolated.

Unit-cell dimensions

The dimensions of the unit cell were determined on the diffractometer. The crystal was mounted along the *b* axis. The 2θ values of 17 reflexions 00*l*, *h*00, *h*0*h* and 0*k*0 (2θ ranging from 10 to 74°) were measured with a precision of 0.01° by using a very narrow counter slit. In the least-squares adjustment of the cell parameters to the sin² θ values, the zero point of the 2θ scale was introduced as an extra variable. This was done separately for the reflexions 0*k*0 as in this case small errors in the height adjustment of the crystal could affect the values obtained for 2θ. The angle β was determined by measuring the φ-difference between the reflexions *h*00 and 00*l*. The observed cell dimensions are listed in Table 1.

The cell dimensions obtained here were compared with a plot of cell dimensions *versus* temperature, measured by Wiebenga (private communication). In this way the temperature was determined to be 100 ± 5°K, in fair agreement with thermocouple measurements.

As some icing occurred during the first day of the intensity measurements the flow rate of the cold nitrogen gas was raised. Because of this the temperature of the crystal during the intensity measurements may have been about 10° lower than during the measurements of the cell dimensions. The results of Coppens & Vos (1971) point in this direction.

Measurements of the intensities

In measuring the intensities the ω-scan technique was applied. The scan width *Z* (in degrees) and the horizontal detector aperture *T* (in mm at 58 mm from the crystal) were calculated according to the formulae

$$Z = 0.27(K + X) + M + 57.3 \tan \theta \cdot \Delta\lambda/\lambda,$$

$$T = K(1 + 0.27 \cos 2\theta) + 0.27X + 114.6 \tan \theta \cdot \Delta\lambda/\lambda.$$

In these formulae *M* is the mosaic spread (in degrees) and *K* and *X* are the dimensions (in mm) of the crystal and X-ray source respectively. The X-ray source is at 215 mm from the crystal. The factor 0.27 in *Z* arises from 360/(215 × 2π) and that in *T* from 58/215. For each crystal used during the data collection the scan width for the reflexion 200 was determined such that 99 per cent of the intensity was recorded under the peak. This yielded a value for the θ-independent part in the first formula after which the scan width for the remaining reflexions could be calculated. The detector aperture *T* could not be varied; a slit of 1.1 × 5.0 mm² was used. The backgrounds as well as the integrated intensities were measured with both the Zr and the Y filter. The backgrounds were recorded at distances of 4° in ω from the peak. In case an unexpectedly high background

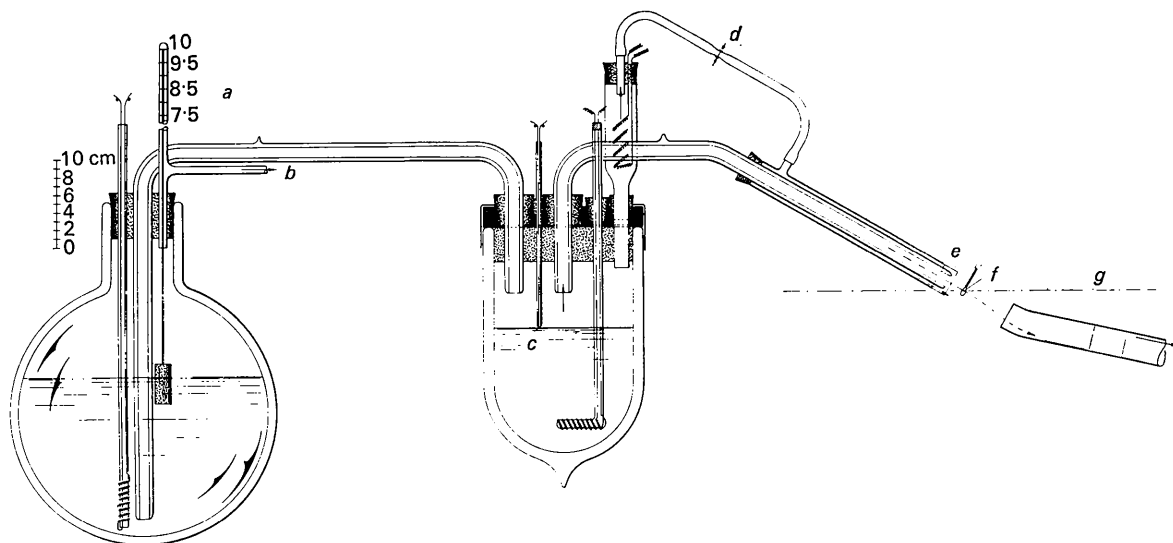


Fig. 2. Low temperature equipment. *a*, Level indicator of storage vessel; *b*, to magnetic valve; *c*, N.T.C. resistance; *d*, control of warm nitrogen; *e*, mylar foil; *f*, crystal; *g*, plane of incident and diffracted beam.

was observed the measurement was repeated at a different ω -value.

The overall stability was tested by measuring a reference reflexion every hour. Moreover every six hours the reflexion 800 was measured to check the stability of the temperature of the crystal. The change in intensity of 800 is 1.2 per cent per degree Centigrade; from 19 measurements it could be concluded that the standard deviation in the temperature is 0.5° .

Three crystals of approximate dimensions 0.6 mm had to be used to collect all reflexions with $\sin \theta/\lambda < 0.8 \text{ \AA}^{-1}$ (965 independent reflexions); the three series were scaled by comparing the intensities of 30 reflexions of medium intensity which had been measured for all three crystals. To make extinction corrections possible, the intensities of the strong reflexions were re-measured for a small crystal (dimensions 0.2 to 0.3 mm) with a relatively large mosaic spread (2°).

Calculation of the intensities, corrections

The intensities of the 770 stronger reflexions were calculated in the usual way from the measured integrated intensities and backgrounds. For the remaining 195 very weak reflexions it appeared to be more accurate to estimate the intensities from the recorded line profiles. For 200 reflexions with intermediate intensities the measurements were done in both ways to determine the scale factor between the two groups of reflexions.

Corrections for the following effects were applied:

- (a) Non-linearity of the detection system; the correction depends on the heights of peak and background and reduces the errors due to non-linearity to 0.2 per cent. (b) Intensity variations with time; corrections as determined from the variation of the reference reflexion were generally less than one per cent. (c) Absorption in the crystal [$\mu\text{Mo} = 1.72 \text{ cm}^{-1}$]. The boundary planes of the crystals were determined accurately, and the absorption corrections were kindly calculated by Dr W. C. Hamilton, Brookhaven. For the three larger crystals the transmission factors in I are between 0.93 and 0.97 and for the smaller one between 0.96 and 0.98. (d) Absorption in the capillary [$\mu(\text{Mo}) = 12.5 \text{ cm}^{-1}$]; the dimensions of the capillaries and the positions of the crystals in the capillaries were measured accurately. To a good approximation the transmission factor A is $A = 1 - F_1(\varphi, \theta) \cdot F_2(\chi, \theta)$, where $F_2(\chi, \theta) = (1 - \sin^2 \chi \sin^2 \theta)^{-1/2}$. $F_1(\varphi, \theta)$ was determined graphically and varied from 0.030 to 0.044 and $F_2(\chi, \theta)$ lies between 1.00 and 1.22. (e) Correction for multiple reflexion and extinction (see below).

Correction for multiple reflexion and for extinction

As \mathbf{b} coincided with the φ axis during the data collection, a reflexion with indices hkl is on the reflexion sphere at the same time as the reflexions $0k0$ and $h0l$, giving rise to the systematic multiple reflexion effects (Burbank, 1965). The corrections to be applied for this effect have been considered by Moon & Shull (1964) and by Coppens (1968a). With the assumptions that

the path lengths of the different beams within the crystal are equal and that the mosaic spread is independent of direction, the correction, ΔI_m , for multiple reflexion is

$$\Delta I_m(hkl) = bf_1 I(hkl)I(0k0) + bf_2 I(hkl)I(h0l) - bf_3 I(0k0)I(h0l).$$

f_1 , f_2 and f_3 are geometrical factors depending on the appropriate Lorentz and polarization factors and can be calculated. The reflexions $h2l$ are especially affected by multiple reflexion because the strong reflexion 020 stays on the reflexion sphere during the measurement of the reflexions $h2l$. Some of these reflexions are listed in Table 3. Corrections for extinction had also to be made. The total correction for extinction and multiple reflexion is:

$$\Delta I_{\text{tot}}(hkl) = aI^2(hkl) + bf_1 I(hkl)I(0k0) + bf_2 I(hkl)I(h0l) - bf_3 I(0k0)I(h0l).$$

The coefficients a and b were determined by comparing the intensities obtained from the small crystal with those from the larger ones. The error in a and b is estimated at 20 per cent.

Table 3. Comparison of some structure factors before and after correction for multiple reflexion

F_o is the uncorrected, F_{cor} the corrected, and F_c the calculated structure factor at the end of the refinement.

h	k	l	F_o	F_{cor}	F_c
0	2	2	94	63	72
0	2	8	48	46	50
2	2	-12	34	29	26
2	2	-2	105	75	58
2	2	0	540	519	501
4	2	-2	57	39	28
4	2	0	314	301	287
8	2	-10	150	142	141
8	2	-2	16	8	10
10	2	-10	101	94	99

Accuracy

The standard deviations in the intensities were calculated from the formula

$$\sigma^2(I) = \sigma_c^2 + 4(0.002I)^2 + (k_1 I)^2 + k_2^2.$$

The first term on the right hand of this equation is the usual variance due to counting statistics, the second term accounts for errors in the corrections (a) to (d) mentioned above; k_1 is zero for measurements without attenuation foils and 0.002 to 0.008 (depending on the attenuation factor used) if attenuation foils are used. For the extra error k_2 only a rough general estimate could be made: k_2 was non-zero when a good deal of white radiation was found at a reflecting position, for reflexions corrected for effect (e), and in cases where the two net backgrounds showed a difference large in comparison with its estimated standard deviation. The standard deviations estimated for the F values are listed in Table 10. After scaling, average values were calculated for the 30 reflexions measured for all three large

crystals. The index $R = \sum |\Delta F| / \sum |F(av)|$, where ΔF is the deviation from the average value $F(av)$, appeared to be 0.005. In general the observed ΔF values show good agreement with the e.s.d. and 42 out of the 90 deviations are lower than $\frac{2}{3}\sigma$. In some cases, however, ΔF is nearly equal to 4σ .

Refinement of the structure

Least-squares refinement

For the refinement of the structure least-squares techniques were generally used; only the hydrogen atoms were located from difference Fourier syntheses. The least-squares program available minimizes the function

$$R' = \sum w \left[F_o - \frac{1}{K} F_c \right]^2,$$

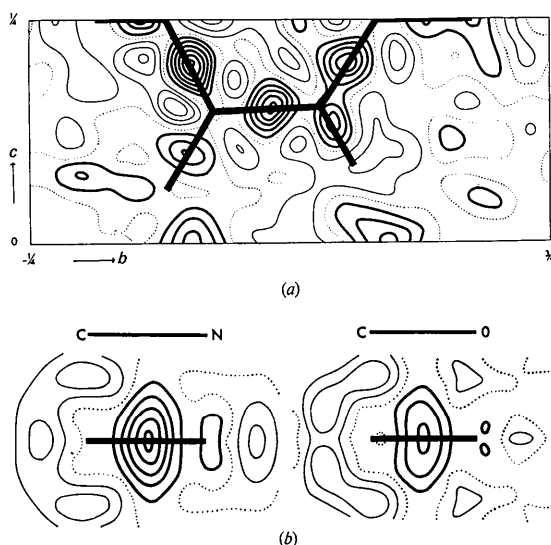


Fig. 3. Difference map of the complete refinement. (a) Section $x=0.25$, (b) average residual density in sections perpendicular to the plane $x=0.25$. Contour lines as in Fig. 1.

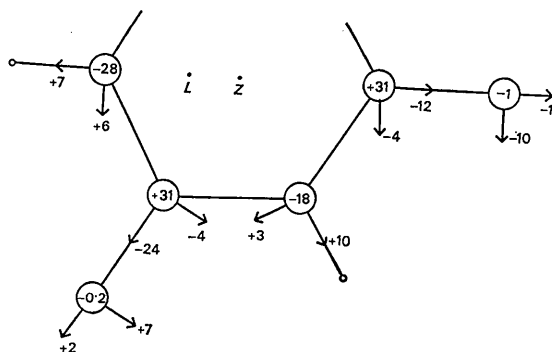


Fig. 4. Differences $U(\text{calc}) - U(\text{obs})$ in units 10^{-4} \AA^2 for the complete refinement. In the circles the differences perpendicular to the plane of the molecule and at the arrows the differences in the radial and tangential directions. Z is the centre of gravity of the molecule, L is the chosen libration centre.

and works in block-diagonal approximation. The thermal vibrations were assumed to be harmonic. For the heavy atoms spherically symmetric scattering factors were used. They were applied in the analytical five-parameter approximation calculated by Moore (1963). The approximation giving the best fit within the copper sphere was considered to be best for the present work. For carbon, $C(\text{valence})$ was used, and for hydrogen a five-parameter representation of the f curve of Stewart, Davidson & Simpson (1965). In the later refinement cycles individual weights w were assigned to the reflexions according to $w=1/\sigma^2$; some very weak reflexions for which the sign of F_o was thought to be uncertain were given zero weight (see Table 10).

After the isotropic refinement a difference map based on $[F_o - F_c(C, N, O)]$ was calculated from which the positions of the hydrogen atoms were determined. In the following least-squares cycles both the positions and isotropic thermal parameters of the hydrogen atoms were refined in addition to the isotropic parameters of the heavy atoms. In this stage of the refinement the hydrogen coordinates were determined again from an $[F_o - F_c(C, N, O)]$ map. The hydrogen parameters from the least-squares refinement lead to a difference of 0.16 Å between the bond lengths $N(2)-H(2)$ and $N(1)-H(1)$; for the hydrogen parameters from the difference map the opposite result is obtained. The average values of the Fourier and least-squares parameters were taken as final coordinates for the hydrogen atoms. In the final cycles of the least-squares refinement the hydrogen parameters were kept fixed whereas the heavy atoms were refined anisotropically. The index R decreased to 0.038. The final parameters are given in Tables 4 and 5. In Table 10 the observed and calculated structure factors based on these parameters are compared. Attempts to use anisotropic thermal parameters for the hydrogen atoms in the least-squares refinement appeared to give unrealistic values for these parameters. The same difficulty was encountered in the full-matrix X-ray refinement by Coppens & Vos (1970).

Table 4. Coordinates and standard deviations

Column A (100°K) without, and column B (100°K) with, libration correction. The standard deviations in parentheses are in units of the last decimal place. For numbering see Fig. 6.

		296°K	A (100°K)	B (100°K)	
C(2)	x	0.2458 (5)	0.24524 (13)	0.24522	
	y	0.1065 (7)	0.10566 (11)	0.10554	
	z	0.1471 (3)	0.14617 (9)	0.14609	
C(1)	y	0.4215 (12)	0.41797 (24)	0.41819	
	N(2)	x	0.2432 (5)	0.24447 (15)	0.24445
		y	0.3107 (6)	0.30893 (11)	0.30907
N(1)	z	0.1501 (3)	0.15034 (8)	0.15026	
	y	0.0116 (10)	0.01140 (13)	0.01130	
	O(2)	x	0.2430 (4)	0.24281 (16)	0.24278
y		0.0153 (6)	0.01341 (9)	0.01332	
O(1)	z	0.0578 (3)	0.05672 (9)	0.05658	
	y	0.5999 (9)	0.59856 (24)	0.59889	
	H(2)	x	0.245	0.243	0.243
y		0.384	0.376	0.376	
z		0.086	0.084	0.084	
H(1)	x	-0.121	-0.122	-0.122	

Table 5. *Vibration parameters (in units 10^{-4} \AA^2), transformed to the orthogonal directions a^* , b and c*

Column *A*: room temperature values, e.s.d. 10–30. Columns *B*, *C* and *D*: low temperature values; *B*, low-order refinement ($\sin \theta/\lambda < 0.63 \text{ \AA}^{-1}$), e.s.d. 4–7; *C*, complete refinement ($\sin \theta/\lambda < 0.80 \text{ \AA}^{-1}$), e.s.d. 2–4; column *D*, calculated values from the rigid body approximation for the complete refinement. For the hydrogen atoms an isotropic temperature factor was applied with $B=1.0$ for H(2) and 1.5 \AA^2 for H(1).

		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
C(2)	U_{11}	280	55	85	116
	U_{22}	240	91	76	65
	U_{33}	230	94	82	65
	U_{12}	0	-2	-3	0
	U_{23}	-10	1	9	-2
C(1)	U_{31}	-10	-2	-2	-2
	U_{11}	440	84	109	139
	U_{22}	230	76	68	56
	U_{33}	330	100	91	88
	U_{31}	60	5	4	3
N(2)	U_{11}	450	135	146	128
	U_{22}	150	70	60	64
	U_{33}	260	70	64	73
	U_{12}	10	0	-1	2
	U_{23}	10	22	12	9
N(1)	U_{31}	0	1	1	0
	U_{11}	390	125	138	110
	U_{22}	240	47	49	56
	U_{33}	220	82	63	69
	U_{31}	-40	-6	-8	0
O(2)	U_{11}	550	139	153	151
	U_{22}	240	91	84	89
	U_{33}	180	71	64	69
	U_{12}	-30	-8	-7	-3
	U_{23}	-30	-7	-9	-12
O(1)	U_{31}	0	1	0	-2
	U_{11}	760	194	200	200
	U_{22}	130	55	56	56
	U_{33}	340	145	137	127
	U_{31}	20	10	10	11

Electron density maps

The residual density map of this refinement with spherical scattering factors is given in Fig. 3. Reflexions with $\sigma(F) > 5$ were not taken into account in the calculation of this map. The densities in the sections perpendicular to the plane of the molecule are average values of the densities belonging to two or three chemically equivalent but crystallographically non-equivalent bonds; the densities above and below the molecular plane were also averaged.

It may be noticed that there are positive regions on the bonds with heights of approximately 0.40 e.\AA^{-3} for C–N, 0.24 for C–O and 0.25 for N–H, whereas there are minima on either side of a bond. These bonding effects will be discussed in a later section.

Analysis of the thermal parameters

For cyanuric acid only little is known about the internal vibrations of the molecule (Shimanouchi & Harada, 1964; it may be noted that an incorrect symmetry has been assigned to the molecule in this paper). Therefore a rigid-body analysis according to Cruickshank's (1956a) method was attempted without making corrections for the contributions of internal vibration. Several

positions of the libration centre on the twofold axis were considered. For each case the thermal parameters based on the rigid-body model, $U(\text{calc})$, were compared with the thermal parameters obtained from the least-squares refinement, $U(\text{obs})$. The best agreement between the $U(\text{calc})$ and $U(\text{obs})$ values was obtained for libration about a point L (0.25, 0.135, 0.25) at a distance of 0.5 \AA from the centre of gravity (Z) in the direction of N(1) (Fig. 4). The translation tensor T and the libration tensor ω calculated from the $U_{ij}(\text{obs})$ values are given in Table 6. The standard deviations in this Table are calculated from the differences between the $U_{ij}(\text{obs})$ values and the $U_{ij}(\text{calc})$ values based on T and ω .

Table 6. *Translation tensor T (in units 10^{-4} \AA^2) and libration tensor ω (in units 10^{-4} rad^2) calculated from the rigid-body approximation*

T_{11}	103 (8)	ω_{11}	6 (1)
T_{22}	56 (5)	ω_{22}	8 (2)
T_{33}	64 (5)	ω_{33}	10 (2)
T_{31}	-2 (5)	ω_{31}	1 (1)

Table 5 shows that the agreement between $U_{ij}(\text{obs})$ and $U_{ij}(\text{calc})$ is rather poor, some differences being as large as ten times the s.d. in $U_{ij}(\text{obs})$. The deviations of the observed vibrations from the rigid-body model are shown schematically in Fig. 4. It is noteworthy that for chemically equivalent atoms analogous values for $U(\text{calc}) - U(\text{obs})$ are observed. This will be discussed further in the section *Discussion*. As the rigid-body treatment is clearly not satisfactory in this case, the libration correction of the atomic coordinates according to Cruickshank (1956b, 1961) is a rough approximation. The corrected coordinates are given in Table 4.

Accuracy

The standard deviations estimated for the atomic coordinates are given in Table 4. These standard deviations include (a) the standard deviations calculated by the least-squares program, (b) shifts due to systematic errors in the correction for extinction and multiple reflexion (an estimate of these shifts was obtained by repeating the refinement with F_o values to which this correction had not been applied) and (c) the estimated errors in the libration correction. For the thermal parameters the standard deviations calculated by the least-squares program are listed. Errors due to effect (b) appeared to be negligibly small. It may be noticed that the errors listed in Tables 4 and 5 do not include systematic deviations due to correlation between atomic parameters and bonding effects.

The random error in the final difference map was calculated with the usual formula:

$$\sigma(D) = \frac{1}{V} [\sum (F_o - F_c)^2]^{1/2} \quad (\text{Cruickshank, 1949}).$$

At large distances from the molecule no significant max-

ima or minima are observed, *e.g.* in the plane $x=0$ all maxima are smaller than 1.6 times the standard deviation, $\sigma(D)=0.06 \text{ e.}\text{\AA}^{-3}$.

Some special refinements

Low-order refinement

To see whether restriction of the reflexions to the copper sphere ($\sin \theta/\lambda < 0.63 \text{ \AA}^{-1}$) would give comparable results, a refinement analogous to that described above for all reflexions was carried out for the 470 appropriate reflexions.

The atomic coordinates of the complete and the low-order refinement are equal within experimental error; the largest shifts (0.0014 \AA on average) are observed for the atoms on the twofold axis. Some thermal parameters showed a highly significant change (see Table 5). In the direction perpendicular to the molecular plane the U values decreased on average, with $28 \times 10^{-4} \text{ \AA}^2$ for C, 12 for N and 10 for O. In the plane of the molecule the U values increased with $11 \times 10^{-4} \text{ \AA}^2$ for C, 8 for N and 5 for O (all values corrected for a small change in the scale factor). For the low-order refinement the rigid-body approximation is even worse than for the complete refinement.

The residual density map of the low-order refinement is shown in Fig. 5. Comparison with Fig. 3 shows that the bonding effects are drastically diminished. A density map of the same reflexions but calculated with the coordinates of the complete refinement gives intermediate results. Apparently for the low-order refinement a strong correlation exists between bonding effects and thermal parameters.

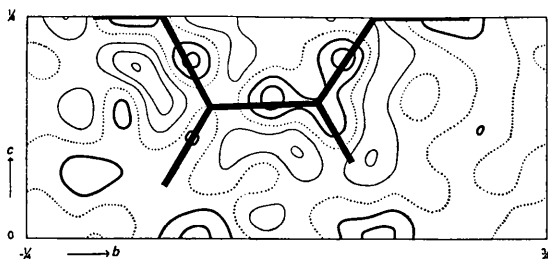


Fig. 5. Difference map of the low-order refinement, $\sin \theta/\lambda < 0.63 \text{ \AA}^{-1}$.

High-order refinement

An unsuccessful attempt was made to refine the scale factor and the parameters of the heavy atoms by use of the high-order reflexions ($\sin \theta/\lambda > 0.5 \text{ \AA}^{-1}$). Later it appeared that this was attributable to the block-diagonal approximation in the least-squares program used. Good convergence was obtained by Coppens & Vos (1971) on repeating the refinement with a full-matrix least-squares program.

Refinement with aspherical scattering factors

Inspection of the temperature parameters of the low-order refinement, the complete refinement and the calculated values based on the rigid-body approximation suggested that in the complete refinement some correlation was still present between bonding effects and temperature parameters. Some preliminary calculations showed that a better approach to a rigid-body model could be obtained by using aspherical atomic scattering factors of atoms in the valence state rather than spherical scattering factors of atoms in the ground state. In the subsequent least-squares refinement a shift of 0.2π -electrons from both carbon and nitrogen to oxygen (obtained from a SCHMO calculation for the π -electrons) was taken into account. Three sp^2 orbitals (P , Q and R) in the plane of the molecule were assigned to each atom and a π orbital perpendicular to this plane. The calculation of the scattering factors (Dawson, 1964b) was based on the following electron-density distribution: carbon $\pi=0.8$, $P=Q=R=1$; nitrogen $\pi=1.8$, $P=Q=R=1$; oxygen $\pi=1.4$, $P=1$, $Q=R=2$ (Q and R are the lone-pair orbitals). At the end of the refinement with aspherical scattering factors the residual R , 0.055, appeared to be higher than the value 0.038 from the spherical refinement. Also the maxima and minima in the difference map appeared to be more pronounced than in the spherical refinement shown in Fig. 3. The fact that the delocalization of the σ -electrons has not been taken into account can explain this poorer agreement. At the oxygen atom, for instance, neither the lone pairs nor the bonding maximum on the C–O bond are accounted for in the spherical model, so that these ‘errors’ may partly compensate each other. In the aspherical model only the lone pairs are considered.

For some of the thermal parameters there appear to be pronounced differences between the spherical and

Table 7. Bond lengths and angles in cyanuric acid at room temperature and at low temperature

The standard deviations in units of the last decimal place are given in parentheses. The sum of the angles at each atom is 360.00° . For numbering see Fig. 6.

	Length			Angle	
	295°K	100°K		295°K	100°K
C(1)–O(1)	1.201 (8) Å	1.217 (2) Å	N(2)–C(1)–N(2')	114.5 (6)°	115.30 (13)°
C(2)–O(2)	1.219 (7)	1.223 (1)	N(2)–C(2)–N(1)	115.8 (4)	115.37 (8)
C(1)–N(2)	1.379 (7)	1.374 (1)	C(1)–N(2)–C(2)	124.7 (4)	124.58 (9)
C(2)–N(2)	1.376 (6)	1.372 (1)	C(2)–N(1)–C(2')	124.3 (6)	124.79 (10)
C(2)–N(1)	1.367 (5)	1.370 (1)	O(2)–C(2)–N(1)	121.9 (4)	121.88 (8)
N(1)–H(1)	0.89	0.90	C(1)–N(2)–H(2)	115	118
N(2)–H(2)	0.92	0.90	N(2)–H(2)–O(2, III)	168	172

aspherical refinements, *e.g.* $U(\text{asph}) - U(\text{sph}) = -0.0045 \text{ \AA}^2$ for nitrogen in the direction perpendicular to the plane of the molecule. For carbon and oxygen the corresponding differences are 5 and $15 \times 10^{-4} \text{ \AA}^2$ respectively. The oxygen atoms move into the direction of the carbon atoms by 0.016 \AA when aspherical scattering factors are used. This stresses again that the values obtained for the structural parameters during a refinement depend on the values used for the scattering factors of the atoms (Dawson, 1964a).

Discussion

Arrangement of the atoms

In Table 7 the bond lengths and angles in the molecule at low temperature are compared with those at room temperature. The standard deviations in the low temperature values are calculated from the e.s.d. in the coordinates (Table 4) and the s.d. in the cell dimensions (Table 1). The fact that the intensities may have been measured at a lower temperature than was used during the determination of the cell dimensions does not affect the values of the bond lengths and angles in the molecule, as the lengths of the *b* and *c* axes depend only slightly on the temperature (Table 1).

It appears that there are no significant differences between the bond lengths at room and low temperature. This is also the case with the lengths of the hydrogen bonds (Table 8). The remaining intermolecular distances become somewhat shorter, however, in going to lower temperatures. Further discussion of the structure will be based on the results of the low-temperature study only. In Fig. 6 the bond lengths and angles in the molecule are indicated. The values observed for cyanuric acid show good agreement with those in other compounds (Table 9). The molecule is approximately planar; the distances of the atoms C(2), N(2) and O(2) from the best plane of the molecule are -0.0025 , -0.0081 and 0.0055 \AA respectively, e.s.d. 0.0012 \AA . The angle with the plane $x = 0.25$ is 1.21° . The arrangement of the molecules in the crystal is shown in Fig. 7. The molecules lie in layers parallel to (100), all molecules showing a small rotation from the (100) plane into the same direction. The molecules within a layer are linked by hydrogen bonds and the layers are held together by van der Waals interactions. From Table 8 and Fig. 7 it may be seen that the C-O groups are in closer contact with molecules of neighbouring layers than the

N-H groups, especially the group C(2)-O(2) which has many close contacts with neighbouring molecules.

Table 8. *Intermolecular distances shorter than 3.120 \AA*

Standard deviations at room temperature *circa* 0.006 \AA , at low temperature *circa* 0.003 \AA .

	295°K	100°K
O(1, I) ----(H)-N(1, II)	2.778	2.778 \AA
O(2, I) ----(H)-N(2, III)	2.812	2.798
O(2, III)----C(2, V)	3.042	2.977
H(1, III)---H(2, VI)	3.09	3.03
O(2, III)---O(1, VI)	3.107	3.047
O(2, III)---C(1, VI)	3.119	3.059
O(2, III)---O(2, V)	3.127	3.065

Hydrogen bonds

The difference in length between the hydrogen bonds $\text{O}(1, \text{I}) \cdots (\text{H})-\text{N}(1, \text{II}) = 2.778 (3) \text{ \AA}$ and $\text{O}(2, \text{I}) \cdots (\text{H})-\text{N}(2, \text{III}) = 2.798 (3) \text{ \AA}$, is large in comparison with the e.s.d. Also infrared work by Newman & Badger (1952) giving N-H---O stretching frequencies of 3210 cm^{-1} for $\text{O}(1, \text{I}) \cdots (\text{H})-\text{N}(1, \text{II})$ and 3060 cm^{-1} for $\text{O}(2, \text{I}) \cdots (\text{H})-\text{N}(2, \text{III})$, shows that the hydrogen bonds are different. From Fig. 8, which shows the location

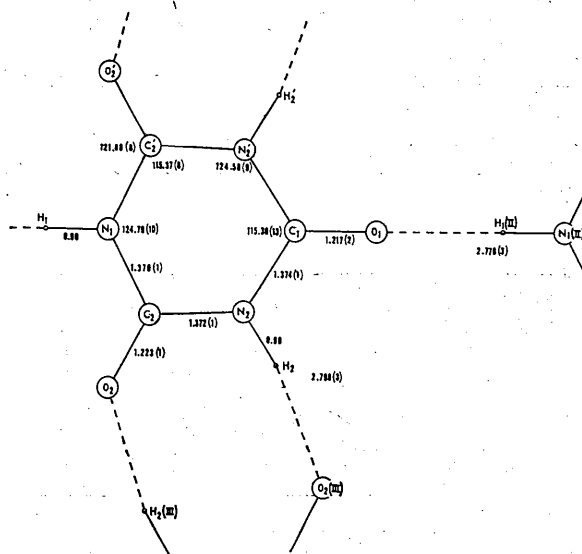


Fig. 6. Bond lengths (\AA) and angles ($^\circ$) at low temperature, with e.s.d.'s in parentheses. The sum of the angles at each atom is 360.00° .

Table 9. *Mean bond lengths and angles in cyanuric acid and related compounds*

The standard deviations of the mean values are given in parentheses in units of the last decimal place.

Compound	C-N	C-O	N-C-N	C-N-C	References
Barbituric acid	1.369 (3) \AA	1.207 (4) \AA	115.1 (4)°	126.5 (3)°	Bolton (1963)
Barbituric acid, 2H ₂ O	1.372 (5)	1.216 (6)	118.0 (7)	125.2 (5)	Jeffrey, Ghose & Warwicker (1961)
Uracil	1.369 (1)	1.230 (2)	114.0 (1)	124.7 (2)	Stewart (1967)
Thymine, H ₂ O	1.372 (4)	1.233 (5)	115.2 (4)	124.6 (3)	Gerdil (1961)
Dilituric acid, 3H ₂ O	1.369 (5)	1.239 (5)	117.1 (2)	125.1 (2)	Craven, Martinez-Carrera & Jeffrey (1964)
Averaged	1.370	1.225	115.9	125.2	
Cyanuric acid	1.372 (1)	1.220 (2)	115.3 (1)	124.7 (1)	This study (low temperature)

of the oxygen lone-pairs as observed in the difference map of Fig. 3, it may be seen that the two hydrogen bonds have a different character. O(1,I)---N(1,II) bisects the lone pairs at O(1) whereas in O(2,I)---N(2,III) only one lone pair at O(2) is involved. Although the difference in electron density of the two lone pairs at O(2) is not significant, it may be noticed that the maximum belonging to the pair in the direction of the hydrogen bond is relatively large. It will be interesting to see whether similar effects occur in other compounds.

Thermal parameters

The short intermolecular contacts and the hydrogen bonds discussed above strongly suggest that the cyanuric acid molecule cannot be considered as free. It was found that the centre of libration is displaced from the centre of gravity by 0.5 Å into the direction of N(1).

The deviations from the rigid-body model, schematically shown in Fig. 4, appear to be rather large, especially in directions perpendicular to the molecular plane. It is tempting to ascribe these deviations to a tendency of the thermal parameters to adjust themselves to a non-spherical electron density distribution in a refinement with spherically symmetric scattering factors. However, also in the neutron diffraction study,

similar deviations from the rigid-body model have been observed (Coppens & Vos, 1970). These deviations may be due to internal vibrations since a relatively large vibration of the nitrogen atoms may possibly be expected as these atoms are at comparatively large distances from the atoms of neighbouring molecules.

Bonding effects

From Table 10 it may be seen that there are still systematic differences between F_o and F_c at the end of the refinement, e.g. in a series of reflexions h,k,l ; $h+2, k,l$; etc. the differences ΔF are alternately plus and minus. Because of these systematic differences the index R at the end of the refinement, 0.038, is larger than the value expected, 0.020, on the basis of the estimated standard deviations of the structure factors. The systematic differences between F_o and F_c give rise to significant maxima and minima in the difference Fourier synthesis of Fig. 3. There are maxima on the bonds, whereas minima appear on either side of a bond. The height of the positive regions is approximately 0.40 for C-N, 0.24 for C-O and 0.25 for N-H; the minima range from -0.16 to -0.29 e.Å⁻³. The systematic arrangement of the maxima and minima suggests that, in comparison with the non-bonded atoms, electron density has moved

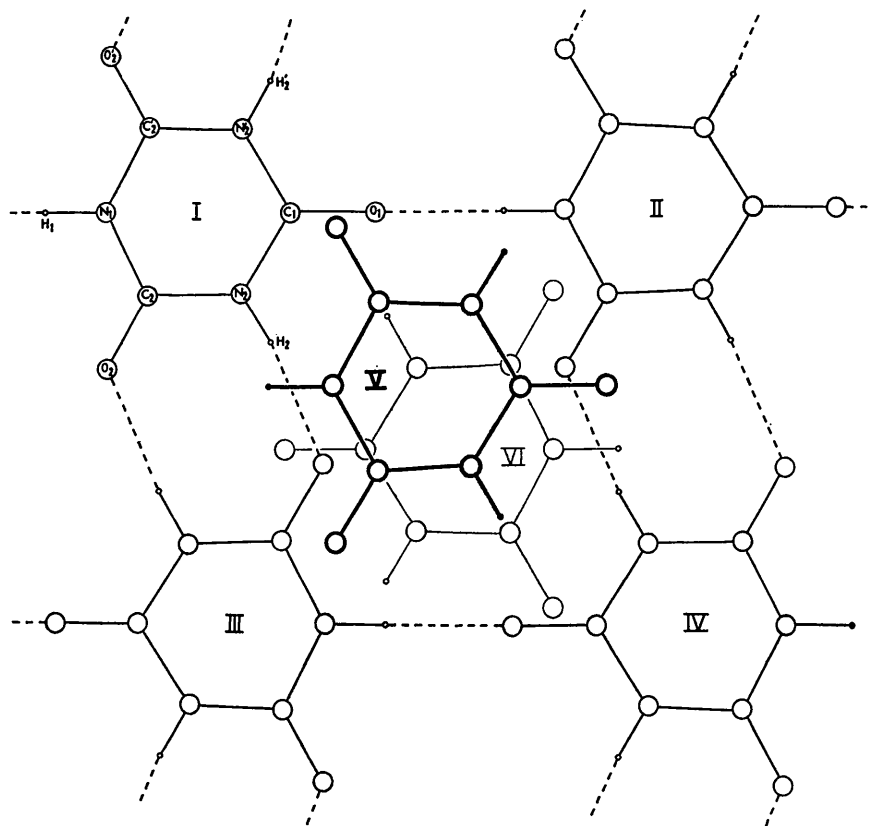


Fig. 7. Perpendicular projection on the yz plane showing the spatial arrangement of the molecules. The six molecules in the Figure have the following coordinates: I, $x y z$; II, $x + y z$; III, $\frac{1}{2} - x \frac{1}{2} - y - z$; IV, $\frac{1}{2} - x \frac{1}{2} - y - z$; V, $1 - x \frac{1}{2} + y \frac{1}{2} - z$; VI, $-x 1 - y - z$.

Table 10. Structure factors and standard deviations of cyanuric acid at low temperature, multiplied by 10

Reflexions with sigma(F) > 5 were not considered in the difference maps and those with sigma(F) = 100 were given zero weight in the least-squares refinements.

Table with columns: h, k, l, F0, Fc, d(F). Multiple rows of numerical data representing structure factors and standard deviations for various reflections.

Table with columns: h, k, l, F0, Fc, d(F). Multiple rows of numerical data representing structure factors and standard deviations for various reflections.

Table 10 (cont.)

Table with columns: h, k, l, F0, Fc, d(F). Multiple rows of numerical data representing structure factors and standard deviations for various reflections.

Table with columns: h, k, l, F0, Fc, d(F). Multiple rows of numerical data representing structure factors and standard deviations for various reflections.

to the centre of the bonds. Perpendicular to the plane of the molecule there are minima of $-0.12 \text{ e.}\text{\AA}^{-3}$ at a distance of approximately 0.7 \AA from the carbon atoms; no significant maxima or minima are found above or below the nitrogen and oxygen atoms. It may be noted that the maxima on the bonds are extended in the π direction.

In the plane of the molecule the difference map shows two maxima of 0.12 and $0.24 \text{ e.}\text{\AA}^{-3}$ at O(2) and two more diffuse maxima of $0.12 \text{ e.}\text{\AA}^{-3}$ at O(1). It may be seen that the lines connecting an oxygen atom with its maximum make angles of about 120° with each other and with the corresponding C-O bond. We are therefore inclined to ascribe these maxima to localized oxygen lone pairs which have not been taken into account during the refinement.

The bonding effects observed in cyanuric acid may be compared with those in other compounds. A review of bonding effects in organic molecules has been given by O'Connell, Rae & Maslen (1966). In general the features discussed in this paper are the same as those observed in cyanuric acid. From the discussion on 1,3,5-triamino-2,4,6-trinitrobenzene it appears that the bonding maxima increase considerably if reflexions with $0.4 < \sin \theta/\lambda < 0.63$ are added to the low-order reflexions. The density maps calculated for cyanuric acid (Figs. 3 and 5) show that a further increase is obtained by considering also the reflexions with $0.63 < \sin \theta/\lambda < 0.8$.

The residual-density map of cyanuric acid has the advantage of having a better resolution than most of the density maps calculated in earlier investigations. It may be noted that the minima at the elongations of the different bonds are separated reasonably well. In the aromatic ring six separate minima are observed, whereas in the centre of the ring the residual density is practically zero. In earlier studies of aromatic compounds which were carried out at room temperature and restricted to reflexions within the copper sphere, the minima in the aromatic ring are rather blurred. It is possible that the hole observed in the centre of some of the aromatic rings is caused by overlap of these blurred minima.

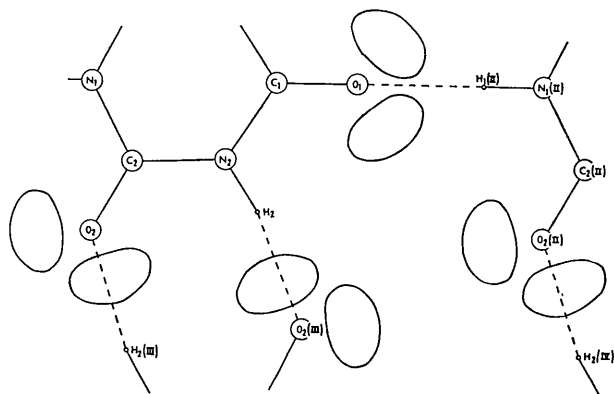


Fig. 8. Schematic drawing of the location of the lone-pair electrons of the oxygen atoms relative to the hydrogen bonds.

This work has been described more extensively in the Doctoral thesis of one of the authors (Verschoor, 1967), which was written under the supervision of Professor E. H. Wiebenga. The authors are much indebted to Professor Wiebenga for suggesting the subject of investigation and for his continuous interest. They thank Professor Aafje Vos for much valuable advice, especially during the interpretation of the results and the preparation of the manuscript. Programs for the refinement with aspherical scattering factors were written by Mrs R. Olthof-Hazekamp. The authors also wish to acknowledge the assistance of Mr M. J. ten Hoor and Mr G. J. Visser in the intensity measurements.

References

- BOLTON, W. (1963). *Acta Cryst.* **16**, 166.
 BURBANK, R. D. (1965). *Acta Cryst.* **19**, 957.
 COPPENS, P. (1968a). *Acta Cryst.* **A24**, 253.
 COPPENS, P. (1968b). *Acta Cryst.* **B24**, 1272.
 COPPENS, P. & VOS, A. (1971). *Acta Cryst.* **B27**, 146.
 CRAVEN, B. M., MARTINEZ-CARRERA, S. & JEFFREY, G. A. (1964). *Acta Cryst.* **17**, 891.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. (1956a). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J. (1956b). *Acta Cryst.* **9**, 757.
 CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
 DAWSON, B. (1964a). *Acta Cryst.* **17**, 990.
 DAWSON, B. (1964b). *Acta Cryst.* **17**, 997.
 FURNAS, T. C. & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**, 449.
 GERDIL, R. (1961). *Acta Cryst.* **14**, 333.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JEFFREY, G. A., GHOSE, S. & WARWICKER, J. O. (1961). *Acta Cryst.* **14**, 881.
 MOON, R. M. & SHULL, C. G. (1964). *Acta Cryst.* **17**, 805.
 MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
 NEWMAN, R. & BADGER, R. M. (1952). *J. Amer. Chem. Soc.* **74**, 3545.
 O'CONNELL, A. M., RAE, A. I. M. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 208.
 POST, B., SCHWARTZ, R. S. & FANKUCHEN, I. (1951). *Rev. Sci. Instrum.* **22**, 218.
 ROLLETT, J. C. (1961). *Computing Methods and the Phase Problem in X-ray Analysis*. Oxford: Pergamon Press.
 SHIMANOUCI, T. & HARADA, I. (1964). *J. Chem. Phys.* **41**, 2651.
 SMITH, P. R. & RICHARDSON, J. W. (1965). *J. Phys. Chem.* **69**, 3346.
 SMITH, P. R. & RICHARDSON, J. W. (1967). *J. Phys. Chem.* **71**, 924.
 SOULES, J. A., GORDON, W. L. & SHAW, C. H. (1956). *Rev. Sci. Instrum.* **27**, 12.
 STEWART, R. F. (1967). *Acta Cryst.* **23**, 1102.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TROTT, B. B. (1960). *J. Sci. Instrum.* **37**, 336.
 VERSCHOOR, G. C. (1964). *Nature, Lond.* **202**, 1206.
 VERSCHOOR, G. C. (1967). Doctoral Thesis, State University, Groningen.
 WIEBENGA, E. H. (1952). *J. Amer. Chem. Soc.* **74**, 6156.
 WIEBENGA, E. H. & MOERMAN, N. F. (1938). *Z. Kristallogr.* **99**, 217.