

Table 4. Al-O bond distances and angles

Al-O bond distances			
Al(1)-O(3)	1.729 Å	Al(2)-O(3)	1.716 Å
Al(1)-O(2)	1.744	Al(2)-O(1)	1.752
Al(1)-O(2)†	1.753	Al(2)-O(4)†	1.779
Al(1)-O(4)*	1.789	Al(2)-O(4)	1.804
Bond angles			
O(3)-Al(1)-O(2)	113.64°	O(3)-Al(2)-O(1)	121.07°
O(3)-Al(1)-O(2)†	104.37	O(3)-Al(2)-O(4)†	111.32
O(3)-Al(1)-O(4)*	118.18	O(3)-Al(2)-O(4)	105.64
O(2)-Al(1)-O(2)†	109.89	O(1)-Al(2)-O(4)†	109.63
O(2)-Al(1)-O(4)*	104.83	O(1)-Al(2)-O(4)	99.38
†O(2)-Al(1)-O(4)*	105.55	†O(4)-Al(2)-O(4)	107.75

The superscripts on the oxygen atoms indicate the positions relative to the basis atoms in Table 2.

* Position $\frac{1}{2} - x, \frac{1}{2} - y, \bar{z}$.

† Position $x, \bar{y}, \frac{1}{2} + z$.

only be achieved after additional electron spin resonance and optical measurements have been performed on the doped sample, when the exact symmetry of the sites should become obvious.

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References

- BOYKO, E. R. & WISNYI, L. G. (1958). *Acta Cryst.* **11**, 444.
 BUSING, W. R., MARTIN, V. O. & LEVY, H. A. (1962). *ORFLS, A Fortran crystallographic least-squares program*. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 COCKAYNE, B. (1966). *J. Amer. Ceram. Soc.* **49**, 204.
 COCKAYNE, B. & ROBERTSON, D. S. (1964). *Solid State Comm.* **2**, 359.
International Tables for X-ray Crystallography (1965). 2nd ed., Vol. III. Birmingham: Kynoch Press.

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A Study of the Crystal structure of β -Cyclotetramethylene Tetranitramine by Neutron Diffraction

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The crystal structure of β -cyclotetramethylene tetranitramine has been reinvestigated by means of neutron diffraction. Least-square refinement of all positional and anisotropic thermal parameters with 545 non-zero reflections yielded a final R value of 0.059. The heavy-atom parameters obtained agree with those from X-ray determinations except for slight position shifts of a few atoms. The positions of the hydrogen atoms have been determined for the first time. All hydrogen atoms are located close to nearby oxygen atoms, a few of which form intramolecular or intermolecular hydrogen bonds of the type C-H...O. Several short intramolecular and intermolecular distances between oxygen and other atoms have been measured.

Introduction

Cyclotetramethylene tetranitramine, known as HMX, is a well-known explosive and a high-melting-point by-product in the manufacture of RDX. β -HMX is the

room temperature stable phase of the four known polymorphic forms, whose crystallographic data are summarized in the paper of Cady, Larson & Cromer (1963). The positions of the heavy-atoms were reported by Eiland & Pepinsky (1955) from a three-dimensional X-ray investigation using an isotropic bulk temperature factor. The same data were further refined by Cady, Larson & Cromer (1963) using anisotropic temperature factors, but hydrogen positions were not reported. In the present work, the structure is reinvestigated to

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locate the hydrogen positions by means of neutron diffraction. Space group $P2_1/c$ is used throughout. The unit-cell constants by Eiland & Pepinsky ($a=6.54$, $b=11.05$, $c=8.70 \text{ \AA}$, $\beta=124.3^\circ$) are used.

Experimental

In the initial stage of the study, only zone data were collected to locate hydrogen positions, since the heavy-atom positions are already reported from X-ray investigations. Two crystals, quite different in size and shape, were selected for data collection. The first one was in the form of a large plate, approximately 4 mm thick, 14 mm wide, and 29 mm long along the crystallographic a axis, from which $0kl$ reflections were collected. The observed intensities of this large crystal were corrected for the complicated absorption effects due to the irregular shape, by normalizing the ob-

served intensity to the incoherent scattering intensity which should suffer the same absorption as the Bragg reflection. The second crystal was roughly a six-sided prism, $3 \times 4 \times 7 \text{ mm}$, with the longest edge parallel to the $[11\bar{2}]$ axis, from which the $[11\bar{2}]$ and $[00l]$ zone reflections were collected. Using these zone data, the hydrogen positions were located by difference Fourier synthesis, but the R value was high unless the heavy atom positions were readjusted.

To investigate all atom positions including heavy atoms, complete three-dimensional data were recollected by using 0.985 \AA wavelength neutrons. The large crystal was machined to a cylindrical shape approximately $4 \times 10 \text{ mm}$ in size with its axis parallel to the crystallographic a axis. The crystal was mounted on a three-dimensional goniometer cradle with the bottom part of the crystal including the goniometer head wrapped with cadmium, thus exposing the upper part

Table 1. Observed and calculated magnitudes of the structure factors for β -HMX

Q indicates the independent scale factors of two different observations. The scale factors are 21.4687 for $Q=1$, and 26.1176 for $Q=2$.

H		K		L		$ F_o $		$ F_c $		Q		H		K		L		$ F_o $		$ F_c $		Q	
1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0

Table 2. Final least-squares parameters of β -HMX with standard deviations

The value of fractional coordinates and the temperature factors are multiplied by 10^4 and 10^5 respectively. The temperature factor is of the form:

$$\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] .$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	-5928 (6)	-21 (4)	-2920 (5)	1092 (141)	504 (37)	651 (63)	61 (63)	148 (90)	242 (45)
N(2)	-3482 (7)	-249 (3)	-2058 (5)	1199 (143)	363 (35)	617 (77)	-62 (53)	281 (87)	7 (38)
N(3)	-188 (6)	1228 (3)	-377 (5)	1366 (136)	277 (34)	566 (73)	-26 (52)	482 (86)	-75 (36)
N(4)	-1092 (7)	2023 (3)	316 (5)	1717 (159)	279 (32)	834 (82)	52 (57)	815 (100)	-39 (39)
O(1)	-6885 (13)	735 (6)	-4182 (10)	1602 (246)	600 (64)	1049 (133)	190 (109)	73 (151)	2 (85)
O(2)	-6991 (13)	-598 (7)	-2372 (9)	1708 (232)	823 (69)	1282 (146)	-237 (111)	1121 (164)	-104 (81)
O(3)	422 (14)	2460 (6)	1818 (10)	3062 (291)	585 (67)	1361 (156)	-53 (118)	1155 (192)	-456 (85)
O(4)	-3290 (13)	2206 (6)	-609 (9)	1883 (279)	603 (68)	1200 (136)	398 (108)	914 (173)	28 (80)
C(1)	-1967 (10)	660 (5)	-2158 (7)	1103 (174)	357 (45)	467 (59)	-27 (90)	456 (122)	-57 (66)
C(2)	2448 (10)	1147 (5)	547 (7)	1865 (205)	247 (48)	755 (108)	-102 (89)	840 (129)	-31 (58)
H(1)	-879 (21)	218 (10)	-2623 (14)	3247 (456)	585 (103)	1081 (204)	27 (176)	1623 (290)	-183 (111)
H(2)	-3146 (21)	1326 (11)	-3223 (15)	2320 (402)	818 (123)	906 (226)	-231 (200)	383 (268)	207 (147)
H(3)	3322 (20)	2031 (11)	1130 (17)	1478 (361)	636 (120)	1961 (267)	80 (184)	310 (266)	-111 (154)
H(4)	2793 (22)	867 (13)	-494 (15)	3518 (502)	1199 (151)	1008 (226)	212 (215)	1520 (301)	-1 (143)

of the crystal (7 mm) to the beam. The integrated intensity was recorded by θ - 2θ step scanning over the entire range of a diffraction peak with a ^3He proportional counter for a preset number of incident neutrons monitored by a transmission-type fission counter. In the first observation, the reflections within $2\theta \leq 50$ degrees were investigated. Later, the measurements were extended to higher scattering-angle reflections ranging up to $2\theta = 65^\circ$.

A total of 668 reflections excluding the extinction reflections by crystal symmetry were examined, among which 551 reflections showed measurable intensity. The observed data were corrected for the Lorentz factors and absorption of the cylindrical crystal with $\mu R = 0.6$, as given by *International Tables for X-ray Crystallography* (1959). To assign an appropriate weight to each reflection individual weight was applied to each observation by counting statistics based on Evans (1961); $\sigma = (T+B) \cdot C / (T-B) L$ where σ , T , B , C , L , are the standard deviations of the observed structure factor, total reflection intensity, background, secondary extinction correction factor $F_c/F_o (= \exp gQ)$, and Lorentz factor respectively. The intense reflections were not used in the early stage of the refinement because of the severe extinction effect. The extinction corrections were applied for all intense reflections whose observed intensities were greater than a certain value (1.6×10^4 in this case) using the linear absorption analogy of the type ' $\exp(-gQ)$ '. The six strongest reflections, which are listed separately in the end of Table 1, were deleted completely from the refinement because the extinction was too severe to apply the single-parameter empirical correction as discussed by Hamilton (1957).

Since the heavy-atom positions are known from previous X-ray investigations (Cady *et al.*, 1963), the hydrogen positions were easily determined by difference Fourier synthesis, in which contributions of heavy atoms were subtracted. Then the least-squares refinement with isotropic temperature factor was carried out, but the R value was still high. Consequently, all atoms were

included in the subsequent refinement. When the R value reached 9%, an anisotropic temperature factor was assigned to individual atoms and the refinement procedure was carried out to the final discrepancy factor $wR = \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2 = 0.059$ and $R = \sum (|F_o| - |F_c|)^2 / \sum F_o^2 = 0.059$. The parameter shift in the last cycle was negligibly small. The final least-squares parameters are given in Table 2 with the estimated standard deviations in parentheses. The refinement was based on the structure factors. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. A set of crystallographic programs, re-edited by Gvildys (1965) and CDC-6400 computer, were used for the least-squares refinement and the calculations of the interatomic distances and bond angles.

Discussion of the structure

The heavy-atom positions determined in this work mostly agree with those reported by Cady, Larson & Cromer (1963), except for a slight shift in the N(2) atom and a lesser shift in the four oxygen atom positions. Accordingly, all bond lengths, except N(2)-N(1) and N(2)-C(2'), agree within estimated standard deviations, as shown in Table 3. Whereas Cady *et al.* reported the N(2)-N(1) distance to be 1.41 Å, or 0.04 Å longer than the N(3)-N(4) distance, our results indicate these distances to be almost the same or the former to be slightly shorter than the latter. This agrees with the corresponding N-N distances of α -HMX as compared in the same Table. The bond angles determined here also show good agreement with the X-ray result, the largest deviation being 2.3° in the N(1)-N(2)-C(1) angle due to the position shift of the N(2) atom. Unlike the X-ray result, the O-N-O angles of the two nitro groups are essentially the same, which is also the case in α -HMX. The bond angles determined in the present study are presented in Table 4. The bond length of β -HMX is compared with that of the α -form, as determined by Cady, Larson & Cromer (1963), in

Table 3. In both forms, the N-C bond lengths range from 1.44 to 1.47 Å for N-C bonds of the ring atoms, and from 1.21 to 1.23 Å for the N-O bonds of the two nitro groups. The two N-N bonds are 1.35 and 1.37 Å in both cases.

Table 3. *Interatomic distances in β -HMX with standard deviations*

The distances reported by Cady *et al.* for β -HMX (CLC) and for α -HMX are given for comparison. The atom designation of α -HMX in the original paper is changed in this Table from N(1), N(2), N(3), H(3), H(4) to N(2), N(3), N(1), H(4), H(3) respectively.

Bond	β -HMX distance		α -HMX distance
	This work	CLC	
N(2)-C(1)	1.448 (7) Å	1.43 Å	1.445 (13) Å
N(2)-C(2')	1.471 (6)	1.45	1.450 (14)
N(3)-C(1)	1.455 (6)	1.46	1.447 (13)
N(3)-C(2)	1.437 (6)	1.43	1.471 (14)
N(2)-N(1)	1.354 (5)	1.41	1.354 (10)
N(3)-N(4)	1.373 (5)	1.37	1.367 (12)
N(1)-O(1)	1.233 (8)	1.22	1.238 (13)
N(1)-O(2)	1.222 (8)	1.23	1.215 (13)
N(4)-O(3)	1.210 (8)	1.22	1.235 (10)
N(4)-O(4)	1.204 (8)	1.22	1.225 (10)
C(1)-H(1)	1.111 (14)	—	1.070 (100)
C(1)-H(2)	1.091 (14)	—	0.830 (90)
C(2)-H(3)	1.101 (15)	—	1.070 (70)
C(2)-H(4)	1.095 (13)	—	0.840 (150)

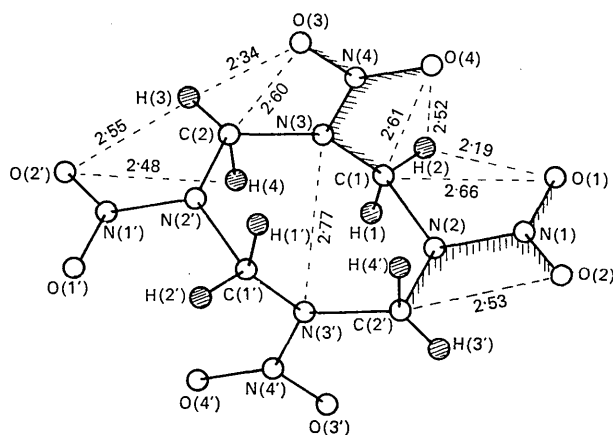


Fig.1. Schematic illustration of the β -HMX molecule with short non-bonded intramolecular distances.

There are two N-NO₂ groups in an asymmetric unit and they are both essentially planar. The plane of the N(1), N(2), O(1), and O(2) atoms is given approximately by the equation $0.2995x - 1.0776y - z = 1.3946$ in the Cartesian coordinate system defined by the crystallographic *a*, *b* axes, and their normal, using the Ångström unit. The C(2') atom is also in this plane but the

Table 4. *Bond angles in β -HMX with standard deviations*

O(1)-N(1)-O(2)	125.9 (6)°	O(3)-N(4)-O(4)	126.7 (5)°
N(2)-N(1)-O(1)	118.0 (5)	N(3)-N(4)-O(3)	115.9 (5)
N(2)-N(1)-O(2)	116.1 (5)	N(3)-N(4)-O(4)	117.4 (5)
N(1)-N(2)-C(2')	115.2 (4)	N(4)-N(3)-C(1)	117.4 (4)
N(1)-N(2)-C(1)	118.2 (4)	N(4)-N(3)-C(2)	118.2 (4)
C(1)-N(2)-C(2')	122.4 (4)	C(1)-N(3)-C(2)	123.8 (4)
N(2)-C(1)-N(3)	113.5 (4)	N(2')-C(2)-N(3)	110.2 (4)
N(2)-C(1)-H(1)	108.5 (7)	N(3)-C(2)-H(4)	107.3 (8)
N(2)-C(1)-H(2)	109.8 (7)	N(3)-C(2)-H(3)	110.5 (7)
N(3)-C(1)-H(1)	106.6 (7)	N(2')-C(2)-H(4)	110.1 (8)
N(3)-C(1)-H(2)	111.8 (7)	N(2')-C(2)-H(3)	109.2 (7)
H(1)-C(1)-H(2)	106.2 (9)	H(3)-C(2)-H(4)	109.6 (11)

Table 5. *Magnitudes of the principal axes of the thermal vibration ellipsoids*

Direction angles, relative to the three orthogonal vectors (*A*₁, *A*₂, *A*₃), of the longest principal axis of the atoms in the two NO₂ groups are also given.

	R.m.s. components ($\times 10^3$)			<i>R</i> ₃ directions		
	<i>R</i> ₁	<i>R</i> ₂	<i>R</i> ₃	<i>A</i> ₁	<i>A</i> ₂	<i>A</i> ₃
N(1)	105 (9) Å	141 (8) Å	210 (7) Å	99 (5)°	97 (4)°	169 (4)°
O(1)	128 (13)	190 (11)	239 (10)	91 (6)	106 (9)	16 (9)
O(2)	122 (16)	181 (11)	230 (10)	88 (6)	124 (9)	146 (9)
N(4)	117 (9)	142 (7)	161 (7)	98 (9)	85 (16)	170 (11)
O(3)	120 (15)	214 (10)	239 (10)	95 (4)	5 (5)	89 (18)
O(4)	129 (14)	177 (10)	216 (11)	94 (6)	31 (12)	121 (12)
N(2)	119 (8)	146 (8)	165 (7)			
C(1)	101 (14)	128 (10)	150 (10)			
N(3)	111 (8)	139 (7)	146 (7)			
C(2)	117 (12)	124 (12)	169 (9)			
H(1)	84 (35)	198 (17)	221 (15)			
H(2)	145 (22)	189 (18)	258 (16)			
H(3)	144 (18)	195 (19)	279 (17)			
H(4)	115 (28)	225 (16)	276 (17)			

C(1) atom is not. The N(3), N(4), O(3), and O(4) atoms are approximately located on the plane $1.0304x + 1.6720y - z = 2.6066$, and C(1) is on this plane but the C(2) atom appears to be off it. The distances of the atoms from each corresponding plane are as follows:

N(2) – nitro group	N(3) – nitro group
N(1) –0.002 Å	N(3) –0.001 Å
N(2) +0.001	N(4) +0.004
O(1) +0.001	O(3) –0.001
O(2) +0.001	O(4) –0.001
C(2') –0.024	C(1) –0.034
C(1) –0.459	C(2) +0.224

It is interesting to notice that among two carbon atoms of each nitramine group, only the carbon atom which is involved in the C–H···O hydrogen bonding (as discussed later) within the same nitramine group is far from the nitro-group plane. This fact may suggest that the uneven orientation of the two carbon atoms within a nitramine group, with respect to the nitro-group plane, is affected considerably by the hydrogen bond. The two neighboring nitro-group planes are almost perpendicular to each other having a dihedral angle of 99°.

The C–H distances range from 1.09 to 1.11 Å. The arrangement of four bonds about the C(2) atom is essentially tetrahedral with the bond angles close to 109 or 110°, as shown in Table 4. However, the bonds about the C(1) atom appear to be slightly distorted from the tetrahedral arrangement in such a way as to give a larger H–C–H angle and a smaller N–C–N angle. In both methylene groups, the H–C–H plane is essentially perpendicular to the N–C–N plane within one degree.

Several non-bonded short intramolecular and intermolecular distances occur in β -HMX. The van der Waals radii are assumed to be 1.57, 1.50, 1.40 and 1.20 Å for carbon, nitrogen, oxygen, and hydrogen atoms respectively. Most of the hydrogen atoms are located close to nearby oxygen atoms in a molecule as shown in Fig. 1. Of these, the H(2)···O(1) distance is particularly short, 2.19 Å, about 0.41 Å shorter than the van der Waals contact. This suggests an intramolecular hydrogen bond of the type C–H···O. The H(3)···O(3) distance is also short, about 0.26 Å shorter than the van der Waals contact, which appears to indicate a weak hydrogen bonding. The C–N ring is shrunken considerably along the N(3)···N(3') direction, (a distance of 2.77 Å) and elongated in the N(2)···N(2') direction (3.94 Å). Comparing these with the corresponding N···N distance of α -HMX measured across the twofold axis at the molecular center, the former is 0.14 Å shorter and the latter is 0.14 Å longer than those of α -HMX.

The two rather short intermolecular C···O distances in β -HMX were reported in the two previous investigations, Cady *et al.* (1963) and Eiland *et al.* (1955). In the present study, it is found that all oxygen atoms in the periphery of a molecule are involved in the short intermolecular distances as shown in Fig. 2. The distances less than 3.20 Å between heavy atoms and those less than 2.60 Å between hydrogen and heavy atoms are presented in the Figure. The closest approach between heavy atoms is observed in the O(3)···C(1) contact (3.02 Å) which occurs between two molecules related to each other by *c* glide mirror symmetry, as are most of the other close contacts between heavy atoms. It is interesting to notice that the N(3) atom in the C–N ring is involved in the close intermolecular con-

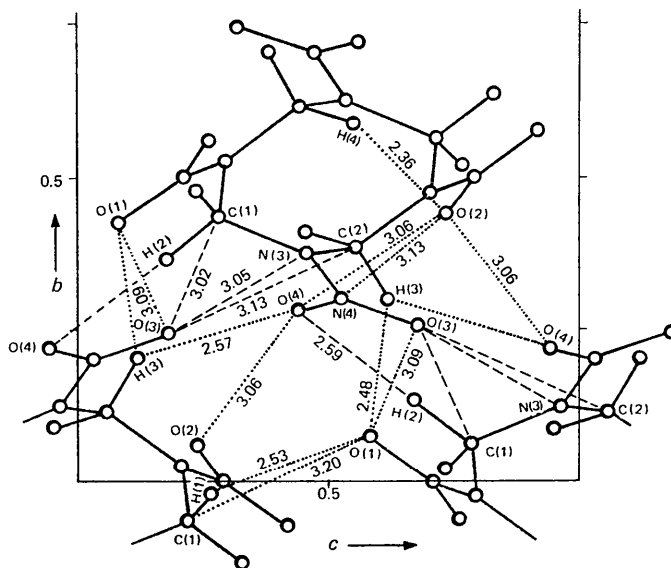


Fig. 2. Projection of β -HMX molecules on the (100) plane showing the short intermolecular distances. The dashed lines indicate the distance between two molecules with the same height and the dotted lines indicate those with different height along the crystallographic *a* axis.

tact [N(3)–O(3) = 3.05 Å], but N(2) is not. Perhaps the shrinkage of the C–N ring along the N(3)···N(3') direction as discussed above may be attributed in part to a probable strain due to the compact packing of molecules along approximately the same direction. All hydrogen atoms are also involved to the short O···H intermolecular contact, where the O(2)···H(4) distance is particularly short, 2.36 Å. It appears to form a weak intermolecular hydrogen bond of the type C–H···O, in which the C···O distance is 3.37 Å and the C–H–O angle is 153 degrees. A similar type of close intermolecular approach of hydrogen atoms and oxygen atoms of nitro groups has been observed in the structure of tetryl and other nitro-compounds, as discussed by Cady (1967).

The anisotropic thermal motion of each atom was examined by converting the thermal parameters in Table 2 into the three components of a root-mean-square displacement from the equilibrium position. The results are given in Table 5. The oxygen and hydrogen atoms which occupy the terminal position of the molecular bond chain exhibit clearly larger vibrations than those of the ring-atoms [e.g. N(2), N(3), C(1), C(2)], as we can expect. The direction of the largest r.m.s. component (R_3) of each atom in the two NO₂ groups is also presented in this Table as evidence of the rigid-body oscillations of the nitro group. Assuming that the N(2), N(1), O(1), O(2) atoms of the N(2)-nitro group are bound by rigid bonds and vibrate collectively about the N(2) atom, the largest vibration direction of an atom 'X' in the NO₂ group should be perpendicular to the direction from the N(2) atom to the 'X' atom if the effect of the anisotropic motion of the N(2) atom is negligible. Consequently the orientation of the largest vibration component is described

by the angles from three orthogonal vectors, A_1, A_2, A_3 , which are defined by N(2)–X, $A_1 \times [O(1)–O(2)]$, and $A_1 \times A_2$, respectively. The vibration directions of the atoms in the N(3)-nitro group are described in the same way. The vibration directions measured from the A_1 direction are essentially 90 degrees for all atoms of the two nitro groups. This supports the assumption of the rigid-body oscillation of the nitro group. The investigation of the deviations from the A_2 and A_3 directions suggest that the nitrogen atom of the NO₂ group oscillates predominantly in the nitro-group plane and the oxygen atoms exhibit a combination of the two predominant motions; in-plane oscillation about the base atom [N(2) or N(3)] and oscillation about the N–N axis.

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References

- CADY, H. H. (1967). *Acta Cryst.* **23**, 601.
 CADY, H. H., LARSON, A. C. & CROMER, D. T. (1963). *Acta Cryst.* **16**, 617.
 EILAND, P. F. & PEPINSKY, R. (1955). *Z. Kristallogr.* **106**, 273.
 EVANS, H. T. J. R. (1961). *Acta Cryst.* **14**, 689.
 GVILDYS, J. (1965). Program MET 153, A FORTRAN Crystallographic Least-Squares Program; Program B-115, A FORTRAN Crystallographic Function and Error Program. Argonne National Laboratory, Argonne, Illinois.
 HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629.
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

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The Behaviour of the Sulphate Groups in the Alum Structures

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Each of the sulphate groups in any alum structure is situated with the sulphur atom and one oxygen atom on a threefold axis and with the other three oxygen atoms in general positions round this axis. The oxygen atoms, and in particular those on the threefold axes, are subject to anomalous behaviour which has been explained by Larson & Cromer in terms of disorder of the sulphate groups. It is shown, however, that the oxygen atoms are more probably subject to extreme thermal motion, the nature of which it is difficult to postulate without violation of the space-group symmetry requirements.

Introduction

Since the completion of the investigations of the alum structures by Lipson & Beevers (1935) and Lipson (1935), interest in the various properties of these

double salts has continued and one of the features that has attracted attention has been the anomalous behaviour of the sulphate groups (Bacon & Gardner, 1958; Larson & Cromer, 1967; Ledsham & Steeple, 1968*a,b*, 1969). In order to conform to the space