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The Crystal Structure of 1,3,5,7-Tetraceto-1,3,5,7-tetrazacyclo-octane

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The crystal of 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclo-octane, $C_{12}N_4O_4H_{20}$, is tetragonal, $a=b=10{\cdot}540$ (2) and $c=12{\cdot}137$ (3) Å, with 4 molecules per unit cell. Systematic absences are consistent with space group $P4_12_12$ (enantiomorphous to $P4_32_12$). The structure was solved by direct methods and refined to a final R index $R_w=0{\cdot}037$ and $R=0{\cdot}039$ for 1244 observed reflections. The molecule consists of alternate CH_2 and N–CO–CH_3 groups in a puckered C–N ring, having a boat shape conformation with a twofold rotation axis through the center of the C–N ring and perpendicular to the mean plane of the puckered ring. The heavy atoms of each acetyl group are essentially coplanar with its neighbouring nitrogen atom. The molecular thermal motion may be represented chiefly by three motions; a libration about the twofold rotation axis and two intramolecular bending motions about the C–C diagonal of the C–N ring.

Introduction

The compound 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclo-octane (TAT) is the tetra-acetyl analog of HMX (cyclo-tetramethylene-tetranitramine) (Bassler, 1943). Recently Siele, Warman & Gilbert (1971) have found three different polymorphic forms of the TAT crystal, two of which are unstable and have been identified mainly by infrared spectra. Here we have determined the crystal structure of the stable form, hereafter called TAT.

Experimental

Colorless crystals of TAT with polyhedral form and many well developed cleavage planes were obtained by slow evaporation of a benzene solution. Preliminary investigation by precession photographs with Mo $K\alpha$ radiation revealed the crystal class to be tetragonal. The crystal data are as follows:

Chemical formula:	$C_{12}N_4O_4H_{20}$
Space group:	$P4_12_12$ or $P4_32_12$ ($P4_12_12$ assumed)
Systematic absences:	$h00$ for $h\neq 2n$ $00l$ for $l\neq 4n$
Cell dimensions:	$a=b=10{\cdot}540$ (2) $c=12{\cdot}137$ (3) Å
Cell volume:	1348·32 Å^3
$Z=$	4 molecules
μ(Mo $K\alpha$)=	0·67 cm^{-1} (based on μ/ϱ by Cromer & Liberman, 1970)
$\varrho_m=$	1·396 g cm^{-3} (Siele, Warman & Gilbert, 1971)
$\varrho_c=$	1·400 g cm^{-3}
λ(Mo $K\alpha$1)=	0·70926 Å (assumed)
$F(000)=$	608 e.

An approximately spherically shaped crystal, 0·50 ± 0·03 mm in diameter, was mounted on an automated 4-circle X-ray diffractometer equipped with a graphite monochromator to reflect Mo $K\alpha$ radiation (Dickens & Bowen, 1971). Preceding the measurement of reflection intensities, the unit-cell dimensions were determined by the least-squares fit to observed 2θ angles of 30 of the most intense reflections having scattering angles greater than 35°. Intensities for reflections in the $+h+k+l$ octant with 2θ values in the range 6 to 70° were measured by θ–2θ continuous scans at 2° per min and the background was counted for 10 sec at both ends of each peak. The diffractometer control program was written by Lenhert (1970). The two equivalent sets of reflections were merged into a unique set of 1742 reflections, of which 1244 reflections were observed and 498 were unobserved, *i.e.* with intensity less than $3\sigma(I)$. The agreement index between the equivalent reflections (hkl) and khl, $\sum\{|F_o hkl - F_o(khl)|/0{\cdot}5\,[F_o(hkl)+F_o(khl)]\}$ was 2·7%. Absorption corrections for a sphere were applied. The maximum and minimum calculated transmission factors were essentially the same, 0·975.

The structure factors were converted to quasi-normalized structure factors (E) by using the *NORMSF* program of the X-ray System (Stewart, 1972). The E statistics, as shown in Table 1, indicate that the structure is acentric, consistent with the space group deter-

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mined from the systematic absences. The initial structure was solved by direct methods using the programs *SINGEN* and *TANGEN* in the *X-RAY* System. Two reflections were selected to establish the origin and enantiomorph (0,1,11, $\varphi=315°$; 0,1,10, $\varphi=0°$). From these two, the phase angles of 14 restricted phase reflections including 4 structure invariant reflections were generated. This subset of reflections was then used for input to the program *TANGEN*. The phase angles of 165 reflections with E larger than 1·4 were generated and refined by application of the tangent formula (Karle & Hauptman, 1956). An E map based upon the phases derived for the 165 reflections revealed the complete C–N ring and part of the acetyl groups. The structure (excluding H atoms) was completed from two more E maps in which the phase angles were determined solely from known atomic positions. The atomic species, particularly the oxygen atoms in the acetyl groups, were identified from their bond lengths. The structure was refined by full-matrix least-squares methods using the program *RFINE* written by L. W. Finger of the Carnegie Institute of Washington. The weighted R index, $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o]^{1/2}$, was reduced to approximately 0·15 on isotropic refinement and to approximately 0·10 on anisotropic refinement. The function minimized in the least-squares refinements was $\sum w(|F_o|-|F_c|)^2$. Scattering factors for the neutral atoms were used and were taken from Cromer & Mann (1968). At this stage, all hydrogen positions were determined from a difference electron-density synthesis. The isotropic temperature factors and the positional parameters of the hydrogens were then refined together with all other atomic parameters. Secondary extinction corrections (Zachariasen, 1968) were applied in the last three cycles of refinement. The weighting scheme was $w_{hkl}=[\sigma_c^2(F_{hkl})+KI_{hkl}]^{-1}$, where $K=3\times10^{-5}$, and $\sigma_c(F_{hkl})$ is the standard deviation based on counting statistics. In the final cycle, $R_w=0{\cdot}037$ and $R=0{\cdot}039$ for the observed reflections. The average shift/error for all parameters was 0·07, the maximum was 0·64. The extinction parameter, γ^* in $F(\text{corrected})=F_{calc}\,(1+\beta\gamma^*|F_{calc}|^2)^{-1/4}$, refined to the reasonable value 0·34 (8)$\times10^{-4}$ cm. The largest secondary extinction correction factor ($F_{corrected}/F_{calc}$) was 0·843 for the 111 reflection. All correlation coefficients were less than 0·41. The largest peak in a difference electron-density synthesis calculated after the final cycle of refinement was approximately 0·2 e.Å^{-3}. There was no observable trend in the values of the function $(1/s)\sum_s w(|F_o|-|F_c|)^2$, where s is the number of reflections in a subset, for subsets of the observed reflections divided into ranges of F and sin θ/λ. The atomic parameters from the final least-squares cycle are given in Table 2. The observed and calculated structure factors are given in Table 3.

Table 1. *Intensity distribution statistics*

The overall temperature factor 3·057 Å^2, obtained by linear isotropic least-squares fit to a Wilson plot, was used in the calculation of normalized structure factors.

	Theoretical (Centric)	Theoretical (Acentric)	Experimental (2D-data)	Experimental (3D-data)
$\langle\|E\|\rangle$	0·798	0·886	0·771	0·858
$\langle E^2\rangle$	1·000	1·000	0·983	1·003
$\langle E^2-1\rangle$	0·968	0·736	0·946	0·777
$\langle(E^2-1)^2\rangle$	2·000	1·000	2·386	1·190
$\langle(E^2-1)^3\rangle$	8·000	2·000	13·898	3·630
$\|E\|>3{\cdot}0$	0·0027	0·0001		0·0021
$\|E\|>2{\cdot}0$	0·0455	0·0183		0·0247
$\|E\|>1{\cdot}6$	0·1096	0·0773		0·0867
$\|E\|>1{\cdot}0$	0·3173	0·3679		0·3556

Description of the crystal structure

Each of the four molecules in the unit cell of TAT is positioned about the (*a*) site of space group $P4_12_12$ (*International Tables for X-ray Crystallography*, 1969) so that the molecule contains a twofold axis perpendicular to the mean plane of the puckered ring. The packing of the TAT molecules is shown in Fig. 1. The shortest distances (less than 3·45 Å) between heavy atoms are O(2)···C(4), 3·138; O(2)···C(6), 3·177; O(2)···N(2), 3·288; O(1)···C(1), 3·364; and O(2)···C(5), 3·416 Å. Thus the C(4) acetyl group has several of the shorter contacts, while the C(3) acetyl group is less constrained.

The molecule of TAT consists of four acetyl groups and four methylene groups alternately linked to form a puckered eight-membered C–N ring (Fig. 2). The

Table 2. *Final least-squares parameters for the structure of TAT*

Thermal parameters have the form

$$\exp\left[-\tfrac{1}{4}(B_{11}a^{*2}h^2+B_{22}b^{*2}k^2+B_{33}c^{*2}l^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl)\right].$$

Atomic coordinates are $\times10^4$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3792 (1)	4718 (1)	1353 (1)	3·49 (6)	2·61 (6)	2·60 (5)	−0·02 (6)	−0·07 (5)	−0·48 (5)
C(2)	5372 (1)	3235 (2)	575 (1)	2·45 (5)	3·22 (6)	3·00 (5)	−0·05 (5)	0·06 (5)	−0·11 (5)
C(3)	4580 (2)	2981 (1)	2497 (1)	3·76 (7)	3·24 (7)	2·91 (5)	−0·65 (6)	−0·41 (5)	0·09 (5)
C(4)	1803 (1)	4022 (1)	443 (1)	2·70 (6)	2·49 (6)	3·68 (6)	0·20 (5)	0·45 (5)	−0·33 (5)
C(5)	5447 (2)	1870 (2)	2660 (2)	4·99 (9)	3·87 (8)	3·74 (7)	−0·04 (7)	−0·72 (7)	0·71 (7)
C(6)	1491 (2)	3249 (2)	1444 (1)	3·92 (8)	3·07 (7)	4·34 (7)	−0·45 (6)	0·83 (6)	0·03 (6)
N(1)	4548 (1)	3568 (1)	1492 (1)	3·07 (5)	2·71 (5)	2·56 (4)	−0·05 (4)	−0·04 (4)	−0·13 (4)
N(2)	2917 (1)	4680 (1)	429 (1)	2·59 (5)	2·54 (5)	2·59 (4)	−0·05 (4)	0·13 (4)	−0·22 (4)
O(1)	3917 (1)	3359 (1)	3255 (1)	6·00 (7)	5·26 (6)	2·86 (4)	0·26 (6)	0·57 (5)	0·35 (5)
O(2)	1107 (1)	4035 (1)	− 360 (1)	3·13 (5)	4·71 (6)	4·51 (5)	−0·51 (5)	−0·78 (4)	0·06 (5)

Table 2 (*cont.*)

Hydrogen atom coordinates ($\times 10^3$) and isotropic temperature factors

H(1)	334 (2)	484 (2)	198 (1)	1·76 (3)
H(2)	436 (2)	543 (2)	119 (1)	1·89 (3)
H(3)	587 (1)	398 (2)	39 (1)	1·34 (3)
H(4)	593 (2)	251 (2)	82 (1)	1·68 (3)
H(5)	555 (3)	168 (3)	336 (2)	6·03 (6)
H(6)	640 (2)	211 (2)	253 (2)	5·34 (5)
H(7)	525 (2)	121 (2)	217 (2)	3·81 (5)
H(8)	211 (2)	246 (2)	150 (1)	4·35 (5)
H(9)	62 (2)	291 (2)	142 (2)	4·29 (5)
H(10)	153 (2)	366 (2)	209 (2)	4·89 (6)

four C atoms of the C–N ring are very closely coplanar with the deviations less than 0·04 Å from the best-fit mean plane (Table 4). The N atoms of the puckered ring deviate from this mean plane by approximately 0·3 Å for atoms N(1) and 0·7 Å for atoms N(2). The heavy atoms in each acetyl group are essentially coplanar with the ring N atom attached to each group. The two ring C atoms adjacent to each acetamide group are also very close to the best-fit plane, with distances less than 0·12 Å for the N(2) group and less than 0·06 Å for the N(1) group. For the N(1) group, the H(1) and H(2) atoms are also located close to the mean plane of the acetyl group, and the non-bonded distances, H(1)···O(1)=2·28 and H(4)···C(5)=2·39 Å, are extremely short. It should be noted, however, that the accuracy of the hydrogen positions is poor because of the small size and the systematic shift of the electron cloud toward the C–H bond, and that these distances may be in error by ~0·1 Å. Bond distances and angles are given in Table 5. In both acetyl groups of the TAT molecule, the C–O bond lengths (average 1·222 Å) indicate double-bond character, and the C–N bond lengths of average 1·366 Å indicate partial double bonding. The C–C bond length, 1·499 (3) Å, is also slightly shorter than a normal C–C single bond. The three bond angles about the C atom of the acetyl groups are almost the same, approximately 120 ± 1·5°, except that the C–C–N angles tend to be 1 to 3° smaller than the other two. The bond angles between the three C–N bonds of each N atom are quite different from each other and range from 116 to 124°.

The symmetrically equivalent pair of C(4) acetyl groups are folded together to give a C(4)···C(4) contact distance of 3·478 Å, and those of the C(3) acetyl groups are stretched out to elongate the molecule. The dihedral angle between the two planes of the N(1) acetyl group pair is 170° and that of N(2) group pair is 53°.

Rigid-body thermal-motion analysis by the method of Schomaker & Trueblood (1968) was applied to the heavy atoms of the molecule, as shown in Table 6. The agreement factor expressed in r.m.s. ΔU_{ij} was 0·004 Å^2 for rigid-body motion of the whole molecule. The average values of $U(I,J)$ principal axes were 0·034 Å^2 for the C–N ring atoms, 0·04 Å^2 for the C(3) and C(4) atoms and 0·053 Å^2 for the C(5), C(6) and O atoms. This is reasonably good agreement considering the fact that each acetyl group has only one linkage to the C–N ring. When the rigid-body motion of the eight atoms of the C–N ring was examined, the agreement was excellent with r.m.s. ΔU_{ij} of 0·0006 Å^2. The average value of $U(I,J)$ components in this case were 0·035 Å^2 for all the eight ring atoms. For the segmental motion of the C–N ring alone, the directions of the libration axes are somewhat related to those of the

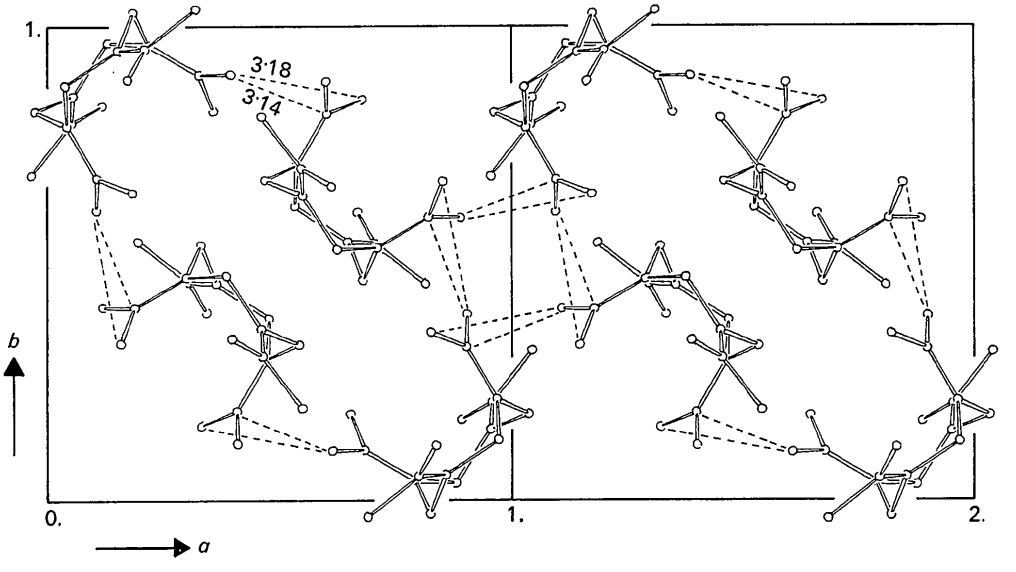

Fig. 1. The molecular arrangement viewed along the *c* axis. Broken lines denote those short intermolecular distances considered to be significantly short.

principal axes of the moment of inertia, I_1, I_2, I_3, where the I_2 axis is the same as the twofold rotation axis and the I_1 and I_3 axes are parallel to the N(2)–N(2) and N(1)–N(1) intramolecular vectors respectively. The C–N ring libration about the axis with the largest moment of inertia (I_1) has the least vibration amplitude

Table 3. *Observed and calculated structure factors for TAT*

Unobserved reflections are indicated by an asterisk. The columns are l, $10F_o$, $10F_c$, $10(w^{-1/2})$, where w is the weighting factor.

Table 4. *Atomic distances from the best-fit mean plane of the acetamide groups and from the mean plane of the* C *atoms in the* C–N *ring*

N(1) group: $0{\cdot}7309x+0{\cdot}6173y+0{\cdot}2910z=6{\cdot}3517$.

Acetamide group	Distance (Å)	Neighboring atoms	Distance (Å)
C(3)	0·0020	C(1)	−0·117
C(5)	−0·0006	C(2)	−0·095
N(1)	−0·0007	H(1)	−0·071
O(1)	−0·0008	H(4)	−0·137

N(2) group: $0{\cdot}4753x-0{\cdot}7910y-0{\cdot}3872z=-2{\cdot}6411$.

Acetamide group	Distance (Å)	Neighboring atoms	Distance (Å)
C(4)	−0·0131	C(1)	−0·024
C(6)	0·0039	C(2)	0·058
N(2)	0·0043	H(2)	−0·254
O(2)	0·0049	H(3)	−0·070

C atoms in C–N ring: $0{\cdot}7107x+0{\cdot}7107y=6{\cdot}3297$.

C atoms in C–N ring	Distance (Å)	Neighboring atoms	Distance (Å)
C(1)	0·0359	N(1), N(1′)	0·327
C(2)	−0·0359	N(2), N(2′)	0·711
C(1′)	0·0359	C(3), C(3′)	0·738
C(2′)	−0·0359	C(5), C(5′)	0·918
		O(1), O(1′)	0·991
		C(4), C(4′)	2·021
		C(6), C(6′)	2·824
		O(2), O(2′)	2·527

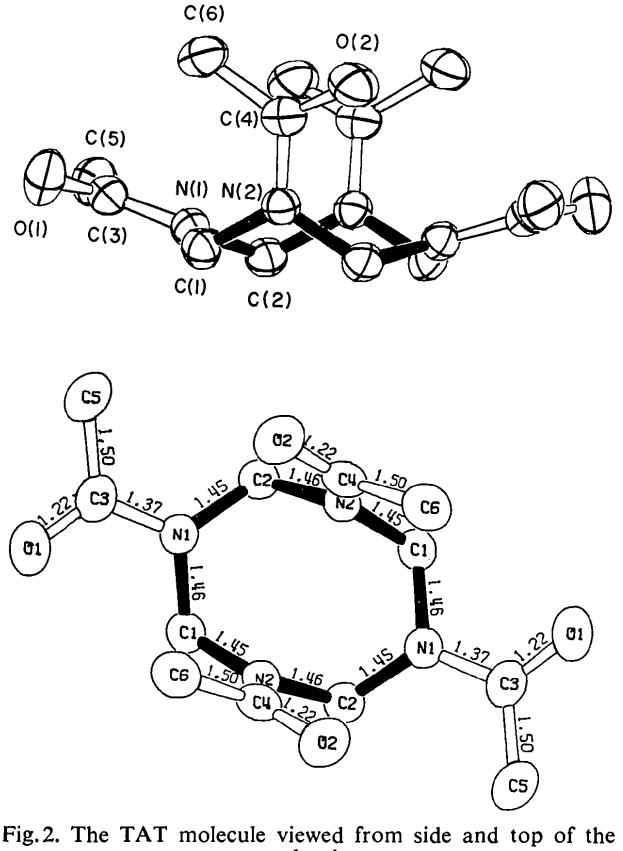

Fig. 2. The TAT molecule viewed from side and top of the molecule.

Table 5. *Interatomic distances and angles in TAT*

C(1)–N(1)	1·460 (2) Å	C(1)–H(1)	0·91 (2) Å
C(1)–N(2)	1·453 (2)	C(1)–H(2)	0·98 (2)
C(2)–N(1)	1·455 (2)	C(2)–H(3)	0·98 (2)
C(2)–N(2)	1·459 (2)	C(2)–H(4)	1·01 (2)
C(3)–N(1)	1·368 (2)	C(5)–H(5)	0·88 (2)
C(3)–C(5)	1·498 (3)	C(5)–H(6)	1·05 (2)
C(3)–O(1)	1·222 (2)	C(5)–H(7)	0·94 (2)
C(4)–N(2)	1·363 (2)	C(6)–H(8)	1·06 (3)
C(4)–C(6)	1·499 (2)	C(6)–H(9)	0·99 (3)
C(4)–O(2)	1·221 (2)	C(6)–H(10)	0·90 (2)
N(1)–C(1)–N(2)	114·4 (1)°	N(1)—C(1)–H(1)	108 (1)°
N(1)–C(2)–N(2)	113·3 (1)	N(1)—C(1)–H(2)	109 (1)
N(1)–C(3)–O(1)	120·6 (2)	N(2)—C(1)–H(1)	109 (1)
N(1)–C(3)–C(5)	119·1 (2)	N(2)—C(1)–H(2)	105 (1)
O(1)–C(3)–C(5)	120·3 (2)	H(1)—C(1)–H(2)	112 (2)
C(6)–C(4)–N(2)	118·4 (1)	N(1)—C(2)–H(3)	108 (1)
C(6)–C(4)–O(2)	121·4 (1)	N(1)—C(2)–H(4)	108 (1)
N(2)–C(4)–O(2)	120·1 (1)	N(2)—C(2)–H(3)	105 (1)
C(1)–N(1)–C(2)	116·0 (1)	N(2)—C(2)–H(4)	111 (1)
C(1)–N(1)–C(3)	119·5 (1)	H(3)—C(2)–H(4)	112 (1)
C(2)–N(1)–C(3)	123·9 (1)	C(3)—C(5)–H(5)	113 (2)
C(1)–N(2)–C(2)	119·0 (1)	C(3)—C(5)–H(6)	112 (1)
C(1)–N(2)–C(4)	123·4 (1)	C(3)—C(5)–H(7)	111 (1)
C(2)–N(2)–C(4)	117·6 (1)	H(6)—C(5)–H(7)	107 (2)
		H(6)—C(5)–H(5)	94 (2)
		H(7)—C(5)–H(5)	118 (2)
		C(4)—C(6)–H(8)	110 (1)
		C(4)—C(6)–H(10)	116 (1)
		C(4)—C(6)–H(9)	112 (1)
		H(8)—C(6)–H(10)	107 (2)
		H(8)—C(6)–H(9)	107 (2)
		H(10)–C(6)–H(9)	104 (2)

and the libration axis with the largest amplitude is approximately parallel to the least inertial axis (I_3).

The rigid-body motions of the acetyl groups cannot be analyzed by the same method, because these groups are planar. However, the orientations of individual thermal ellipsoids in the acetyl groups indicate that the smallest amplitudes are always directed toward the attached N atom in the ring. This is consistent with segmental libration of the acetyl groups, rather like the segmental motion of the nitro group found in several compounds, *i.e.* β-HMX (Choi & Boutin, 1970) and *s*-trinitrobenzene (Choi & Abel, 1972).

The L_1 axis (with the largest amplitude) and the L_3 axis (with the smallest amplitude) of the molecular libration (based on whole molecule) are essentially parallel to C(2)–C(2) and C(1)–C(1) intramolecular vectors respectively, and are shifted from the center of mass toward the corresponding C–C vector in the molecule by 0·545 for L_1 and 0·722 Å for L_3 axis. Thus the distance of L_3 axis from the C(1)–C(1) vector is only 0·10 Å and that of L_1 axis from the C(2)–C(2) vector is 0·23 Å. The departure of L_1 and L_2 axes from the center of mass toward the C–C diagonals of the puckered C–N ring suggests that the oscillations about the L_1 and L_3 axes may be intramolecular bending motion rather than libration of the rigid molecule. The L_2 axis of the molecular libration is coincident with the twofold rotation axis of the molecule.

The TAT molecule is very similar to α-HMX (Cady, Larson & Cromer; 1963). Both have boat shape con-

Table 6. *Rigid-body motion of TAT*

All tensors are presented in the crystal coordinate system. The direction cosines of the principal axes of each motion are given in the special coordinate system specified. The C–C system coordinate axes are defined by choosing the molecular rotation axis as the X axis and the C(1)–C(1) intramolecular vector as the Y axis. In the N–N system, N(2)–N(2) vector is chosen as the Y axis.

WHOLE MOLECULE

$$\mathbf{T}\ (\text{Å}^2): \begin{pmatrix} 0.0318 & -0.0036 & 0.0020 \\ -0.0036 & 0.0318 & -0.0019 \\ 0.0020 & -0.0019 & 0.0348 \end{pmatrix}$$

C–N RING

$$\begin{pmatrix} 0.0270 & -0.0069 & 0.0018 \\ -0.0069 & 0.0270 & -0.0018 \\ 0.0018 & -0.0018 & 0.0319 \end{pmatrix}$$

Principal axes of **T**:

(C–C system)

0·1946 Å	0·0009	0·3320	0·9433
0·1797	0·0030	0·9433	−0·3320
0·1681	1·0000	0·0027	0·0004

(N–N system)

0·1887 Å	0·0001	−0·5521	0·8338
0·1736	0·0030	0·8338	0·5521
0·1418	1·0000	0·0000	0·0000

$$\mathbf{L}\ (\text{radian}^2) \begin{pmatrix} 0.0022 & -0.0002 & 0.0002 \\ -0.0002 & 0.0022 & -0.0002 \\ 0.0002 & -0.0002 & 0.0018 \end{pmatrix}$$

$$\begin{pmatrix} 0.0030 & -0.0017 & 0.0007 \\ -0.0017 & 0.0030 & -0.0007 \\ 0.0007 & -0.0007 & 0.0057 \end{pmatrix}$$

Principal axes of **L**:

(C–C system)

L_1	2·89°	0·0025	0·0155	0·9999
L_2	2·54	0·9998	0·0182	0·0009
L_3	2·32	0·0164	−0·9997	0·0155

(N–N system)

L_1	4·55°	0·0002	0·1700	−0·9854
L_2	3·71	0·0012	0·9854	0·1700
L_3	2·04	1·0000	0·0000	0·0000

formations with a twofold rotation axis through the molecular center. The bond lengths and angles found here for the C–N ring generally agree with those of α- and β-HMX (Cady *et al.*, 1963; Choi & Boutin, 1970), except that the variation among the chemically equivalent bonds is much less in TAT than in the HMX molecules.

References

Bassler, G. C. (1943). Thesis. Pennsylvania State College, Pa.

Cady, H. H., Larson, A. C. & Cromer, D. T. (1963). *Acta Cryst.* **16**, 617–623.

Choi, C. S. & Boutin, H. P. (1970). *Acta Cryst.* B**26**, 1235–1239.

Choi, C. S. & Abel, J. E. (1972). *Acta Cryst.* B**28**, 193–201.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Dickens, B. & Bowen, J. S. (1971). *Acta Cryst.* B**27**, 2247–2255.

International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.

Karle, J. & Hauptman, H. (1956). *Acta Cryst.* **9**, 635–651.

Lenhert, P. G. (1970). Winter Meeting, American Crystallographic Association, Tulane University, New Orleans, Louisiana.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Siele, V. I., Warman, M. & Gilbert, E. E. (1971). Private communication.

Stewart, J. M. (1972). X-ray System, Technical Report TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1973). B**29**, 656

Etude de la Structure Cristalline du Sulfite de Magnésium Hexahydraté, $MgSO_3.6H_2O$

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$MgSO_3.6H_2O$ crystallizes in the space group $R3$ with $a=8{\cdot}830$ and $c=9{\cdot}075$ Å; $Z=3$ (hexagonal axes). The structure has been refined to an R value of 0·059 using three-dimensional diffractometer data. The structure consists of a slightly distorted CsCl arrangement of octahedral $[Mg(H_2O)_6]^{2+}$ and pyramidal SO_3^{2-} ions.

Introduction

A la suite des expériences de résonance paramagnétique sur des cristaux de sulfite de magnésium hexahydraté ($MgSO_3.6H_2O$) dopés avec des ions Mn^{2+}, il a été possible, pour Fontana & Lacroix (1966), de calculer l'orientation de l'octaèdre des molécules d'eau autour de l'atome de manganèse. Pour effectuer ces calculs, il fallait faire des hypothèses sur les signes absolus de deux constantes de l'Hamiltonien de spin.