

## The Structure of 3,4,5-Trichlorotetracyclo[4.4.0.0<sup>3.9</sup>.0<sup>4.8</sup>]decan-2-one, a Novel Cage Molecule

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The crystal structure of the novel cage molecule, 3,4,5-trichlorotetracyclo[4.4.0.0<sup>3.9</sup>.0<sup>4.8</sup>]decan-2-one, C<sub>10</sub>H<sub>9</sub>Cl<sub>3</sub>O, has been determined from automatic diffractometer data. The structure was refined by anisotropic least squares to a final *R* value of 7.3% for 1168 observed reflections. The space group is *P*2<sub>1</sub>/*c* with *Z*=4 and cell dimensions *a*=7.562, *b*=13.183, *c*=10.233 Å, β=94.40°. All hydrogen atoms were found and their positions refined. The almost spherical molecules are arranged in hexagonal close-packing, with the pseudo-hexagonal layers parallel to (001). The thermal parameters were analyzed for rigid body motion and gave nearly isotropic translational and rotational tensors, corresponding to r.m.s. amplitudes of 0.2 Å and 3.4°, respectively.

### Introduction

A novel cage system with the chemical composition C<sub>10</sub>H<sub>9</sub>Cl<sub>3</sub>O was recently reported by Stedman, Miller & Hoover (1966), who concluded from the method of synthesis and spectral data that the new compound was most likely the 3,4,5-trichlorotetracyclo[4.4.0.0<sup>3.9</sup>.0<sup>4.8</sup>]decan-2-one shown in Fig. 1. The conformation of the C-Cl bond on C(5) was not known. The crystal structure was determined in order to verify the configuration of the cage, to clarify the stereochemistry at C(5), and to obtain detailed information about the geometry of the molecule.

### Crystal data

The crystals were grown by Mrs L.S. Miller of the Smith Kline and French Laboratories in a form suitable for the structure determination. The space group was determined by means of precession photographs

with Mo *K*α radiation. The lattice constants were measured on a Picker automated single-crystal diffractometer, with Cu *K*α radiation, and refined by least squares. The density was measured by the flotation method.

3,4,5-Trichlorotetracyclo[4.4.0.0<sup>3.9</sup>.0<sup>4.8</sup>]decan-2-one, C<sub>10</sub>H<sub>9</sub>Cl<sub>3</sub>O, M.W. 251.54.

Monoclinic, space group *P*2<sub>1</sub>/*c*, from systematic absences: *h*0*l* absent for *l*=2*n*+1, 0*k*0 absent for *k*=2*n*+1.

*Z*=4

*a*=7.562 (σ=0.002), *b*=13.183 (σ=0.004), *c*=10.233 (σ=0.003) Å.

β=94.40 (σ=0.03)°.

*D*<sub>m</sub>=1.683 (σ=0.007) g.cm<sup>-3</sup>

*D*<sub>x</sub>=1.643 g.cm<sup>-3</sup>

μ<sub>Cu Kα</sub>=77.89 cm<sup>-1</sup>.

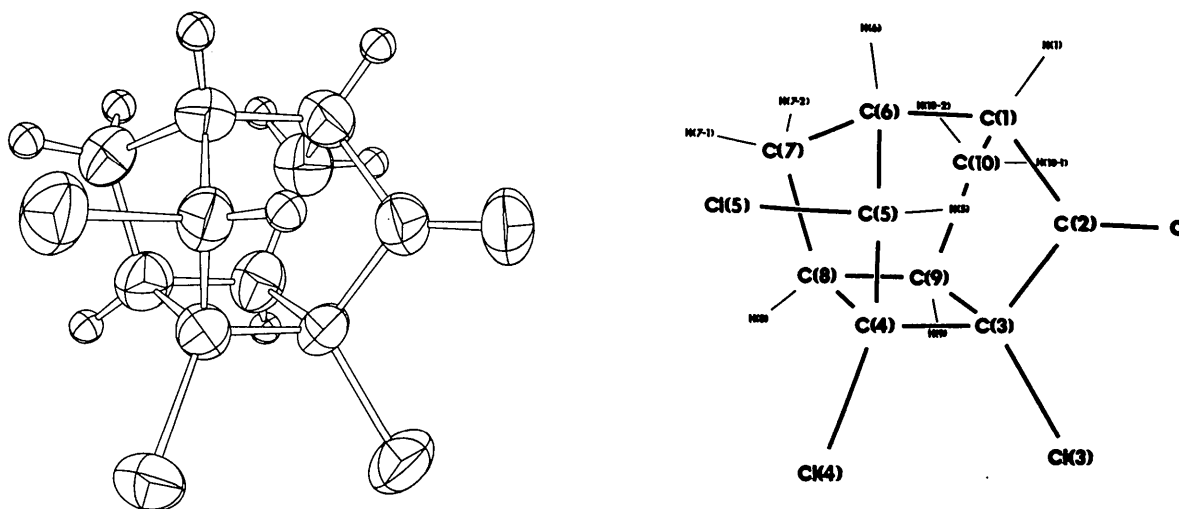


Fig. 1. View of the molecule, and identification of the atoms.

Since the space group is centrosymmetric and the molecule non-centrosymmetric, the crystal structure must be racemic.

### Experimental

The intensity data were measured on a Picker four-circle automated single-crystal diffractometer with Cu  $K\alpha$  radiation. The crystal showed the morphological forms  $\{110\}$  and  $\{011\}$ . Its dimensions, which were measured on an optical goniometer with a ruled grating, were between 0.11 and 0.22 mm. The crystal faces were analytically described in a Cartesian coordinate system with  $x||a^*$ ,  $y||b$ ,  $z||c$ , by the following equations:

$$\{110\}: S_h 0.867x + S_k 0.498y = 0.098 \text{ mm}$$

$$\{011\}: S_l 0.057x + S_k 0.613y + S_l 0.788z = 0.056 \text{ mm.}$$

$$S_h = \text{sign}(h) \quad S_k = \text{sign}(k) \quad S_l = \text{sign}(l).$$

The coefficients of  $x, y, z$  (*i.e.* the direction cosines of the face normal) were calculated with the use of the measured lattice constants.

The intensities were measured up to  $\sin \theta/\lambda = 0.588 \text{ \AA}^{-1}$ , ( $\theta = 65^\circ$ ), using the diffractometer in the  $\theta$ - $2\theta$  scanning mode. The scanning range was  $1^\circ$  in  $\theta$ , with a speed of  $1^\circ$  per minute. The background was measured by a stationary count for 20 seconds on either side of the peak. Most of the high-order reflections were weak, since the intensities decreased rapidly with  $\theta$ . These weak intensities were remeasured with a scanning speed of  $\frac{1}{3}^\circ$  per minute and the background was measured for 40 seconds. Nevertheless, an appreciable proportion of the intensities were unobserved. All the accessible symmetry related reflections  $hkl$  and  $h\bar{k}l$  were measured and the mean value was used to calculate the structure amplitudes. The intensities were corrected for absorption using a general absorption program for an IBM 1620 computer (Craven, 1963). There was no indication that extinction corrections were required. Of the 1691 independent reflections accessible on the diffractometer with Cu  $K\alpha$  radiation, 1168 were observed above the background.

### Determination of the structure

The structure amplitudes (uncorrected for absorption) were converted to normalized  $|E_{hkl}|$  values and used in the IBM 1620 sign correlation procedure developed by Beurskens (1963). This led to two different sets of signs for 360 structure factors, one of which was strongly favored by the probability criterion of Cochran & Woolfson (1955). The three-dimensional  $E$  map calculated with this set showed one very high peak, which was also an obvious solution of the Patterson  $E^2 - 1$  synthesis, but no peaks in the Patterson map corresponding to other weaker peaks in the  $E$  map could be identified. The  $E$  map calculated with the less probable set of signs, however, showed three strong

peaks that were identified as the positions of the chlorine atoms and explained nearly all features of the Patterson synthesis.

A Fourier synthesis (Shiono, 1965) with signs determined by these chlorine positions revealed all the carbons and the oxygen, and a subsequent structure factor calculation gave an  $R$  value of 0.35 for all observed reflections. The refinement was then carried out by least squares (Busing, Martin & Levy, 1962), using weights  $w = 1/\sigma^2$  with  $\sigma(|F|) = \frac{1}{2}|F_{\min}| + 0.05|F|$ ,  $|F_{\min}| = 50$  (Table 4). After two cycles of isotropic and two cycles of anisotropic refinement, the  $R$  value was 0.09. A difference Fourier synthesis showed several strong peaks, but did not reveal the hydrogen atoms unambiguously. The structure factors were therefore corrected for absorption as described above. The square roots of the calculated transmission factors lay between 1.93 and 1.40. An anisotropic least-squares refinement with these corrected data gave no change in the  $R$  value and variations in the atomic positions of the order of  $\sigma$ . However, the difference map now showed nine strongest peaks which could be identified as the hydrogen atoms.

Two more least-squares cycles, refining the positional and anisotropic thermal parameters of chlorine, carbon, and oxygen, and the positional parameters of hydrogen reduced the  $R$  value to 0.073. The thermal parameters of the hydrogens were assumed to be the same as those of the carbon atoms to which they were attached and they were not varied. The positional parameters of the hydrogens did not change more than 0.5 $\sigma$  in the second cycle. The atomic positional and thermal parameters are given in Tables 1, 2 and 3, the observed and calculated structure factors in Table 4.

Table 1. Fractional atomic coordinates

The estimated standard deviations given in parentheses refer to the last decimal position.

	$x$	$y$	$z$
C(1)	0.4782 (7)	0.1209 (4)	0.3231 (6)
C(2)	0.4485 (7)	0.0064 (4)	0.3136 (5)
C(3)	0.3043 (7)	-0.0032 (3)	0.2015 (5)
C(4)	0.1323 (6)	0.0497 (4)	0.2397 (5)
C(5)	0.1670 (7)	0.0895 (4)	0.3819 (5)
C(6)	0.3010 (7)	0.1723 (4)	0.3601 (5)
C(7)	0.2127 (8)	0.2293 (4)	0.2423 (6)
C(8)	0.1687 (8)	0.1408 (4)	0.1492 (5)
C(9)	0.3408 (7)	0.0885 (4)	0.1091 (6)
C(10)	0.5078 (8)	0.1393 (5)	0.1771 (6)
O	0.5260 (5)	-0.0608 (3)	0.3715 (4)
Cl(3)	0.2887 (2)	-0.1260 (1)	0.1356 (2)
Cl(4)	-0.0664 (2)	-0.0172 (1)	0.2068 (2)
Cl(5)	-0.0291 (2)	0.1406 (1)	0.4453 (2)
H(1)	0.583 (8)	0.132 (5)	0.390 (6)
H(5)	0.214 (8)	0.038 (5)	0.454 (6)
H(6)	0.326 (8)	0.212 (5)	0.440 (6)
H(7-1)	0.112 (9)	0.272 (5)	0.273 (6)
H(7-2)	0.310 (9)	0.277 (5)	0.210 (6)
H(8)	0.081 (9)	0.156 (5)	0.077 (7)
H(9)	0.355 (8)	0.069 (5)	0.011 (7)
H(10-1)	0.630 (9)	0.108 (5)	0.151 (7)
H(10-2)	0.539 (9)	0.215 (6)	0.154 (7)

Table 2. *Anisotropic thermal parameters*The temperature factor expression used was  $B = \sum_{ij} \beta_{ij} h_i h_j$ .

The estimated standard deviations given in parentheses refer to the last decimal position.

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	0.0145 (10)	0.0055 (4)	0.0107 (6)	-0.0004 (5)	-0.0013 (6)	0.0003 (4)
C(2)	0.0173 (10)	0.0056 (4)	0.0087 (6)	0.0020 (5)	-0.0016 (6)	-0.0001 (4)
C(3)	0.0188 (10)	0.0033 (3)	0.0094 (6)	0.0010 (4)	-0.0013 (6)	-0.0008 (3)
C(4)	0.0132 (9)	0.0040 (3)	0.0105 (6)	-0.0006 (4)	-0.0008 (6)	0.0012 (3)
C(5)	0.0157 (10)	0.0047 (3)	0.0084 (5)	0.0016 (4)	0.0003 (6)	-0.0004 (3)
C(6)	0.0147 (9)	0.0049 (3)	0.0104 (6)	-0.0007 (5)	-0.0005 (6)	-0.0010 (4)
C(7)	0.0201 (12)	0.0042 (3)	0.0119 (7)	0.0008 (5)	0.0006 (7)	0.0000 (4)
C(8)	0.0204 (12)	0.0050 (3)	0.0095 (6)	0.0005 (5)	-0.0007 (7)	0.0003 (4)
C(9)	0.0203 (12)	0.0054 (4)	0.0093 (6)	0.0011 (5)	0.0018 (7)	0.0007 (4)
C(10)	0.0181 (11)	0.0068 (4)	0.0109 (7)	0.0002 (6)	0.0029 (7)	0.0006 (4)
O	0.0228 (9)	0.0065 (3)	0.0117 (5)	0.0046 (4)	-0.0027 (5)	0.0007 (3)
Cl(3)	0.0314 (4)	0.0043 (1)	0.0125 (2)	0.0015 (1)	-0.0007 (2)	-0.0018 (1)
Cl(4)	0.0162 (3)	0.0057 (1)	0.0160 (2)	-0.0026 (1)	-0.0034 (2)	0.0000 (1)
Cl(5)	0.0171 (3)	0.0058 (1)	0.0151 (2)	0.0010 (1)	0.0042 (2)	-0.0005 (1)

Table 3. *R.m.s. displacements U along principal axes of thermal ellipsoids*

	$U_1$	$U_2$	$U_3$
C(1)	0.1952 Å	0.2190 Å	0.2489 Å
C(2)	0.1895	0.2167	0.2532
C(3)	0.1645	0.2081	0.2522
C(4)	0.1778	0.1907	0.2482
C(5)	0.1865	0.2080	0.2303
C(6)	0.1887	0.2145	0.2430
C(7)	0.1904	0.2400	0.2524
C(8)	0.2058	0.2196	0.2516
C(9)	0.2081	0.2219	0.2487
C(10)	0.2156	0.2391	0.2544
O	0.1807	0.2548	0.2987
Cl(3)	0.1812	0.2580	0.3105
Cl(4)	0.1810	0.2400	0.3064
Cl(5)	0.2022	0.2344	0.2876

### Description of the structure

The configuration of the molecule (Fig. 1) is as proposed by Stedman *et al.* (1966). It has a ten-carbon cage structure containing one four-membered, two five-membered and two six-membered saturated rings. The C(5)–Cl(5) bond points away from the carbonyl group, in the conformation of least steric repulsion with respect to the substituents of the C(1)–C(2)–C(3)–C(4)–C(5)–C(6) ring.

The cyclobutane ring C(3)–C(4)–C(8)–C(9) is a planar square within the limits of accuracy. The deviations of the angles from 90° are equal to  $\sigma$ , and the distances of the atoms from the least-squares plane are less than 0.003 Å. The cyclopentane rings C(1)–C(2)–C(3)–C(9)–C(10) and C(4)–C(5)–C(6)–C(7)–C(8) are puckered with internal angles varying between 97 and 106°. The angles tend to be greater in the latter ring than in the former, possibly owing to the repulsion of Cl(5) and H(7–1). The two cyclohexane rings are in boat form with internal angles close to tetrahedral (108 to 111°), except for those at the atoms C(2) and C(5), C(7) and C(10), which are close to 100°. The angles of the C(1)–C(6)–C(7)–C(8)–C(9)–C(10) ring are all greater than those of the C(1)–C(2)–C(3)–C(4)–C(5)–C(6) ring, owing to the repulsion of H(7–2) and

H(10–2). The carbonyl group is planar within the limits of accuracy, and the sum of bond angles around C(2) is 359.9°.

The C–C bond lengths vary between 1.517 and 1.574 Å, *i.e.* over a range of about  $7\sigma$ , with a mean value of 1.545 Å. There are some systematic differences which lie in the probably significant range from 2 to  $4\sigma$ , and might arise from the angular distortions necessary to form the cage. The bonds in the cyclobutane ring are all longer than the mean value and one of them, C(3)–C(9), is longer by about  $4\sigma$ . The longest bond observed, C(1)–C(6), at 1.574 Å, is that which is opposite to the cyclobutane ring. Together with two sides of that ring, it links the two cyclopentane rings to form the cage. The bonds C(3)–C(4) and C(4)–C(5) are both longer than the mean at 1.552 and 1.550 Å and both have adjacent C–Cl bonds at both ends. The other seven C–C bonds are either equal to or less than the mean value. No systematic correlation could be found between these variations in distances and the angular distortions from 109°28'. The C–O bond has a normal value. Of the three C–Cl bonds, C(5)–Cl(5) is 0.04 Å longer than the other two, for which the only distinction is that it involves one of the carbon atoms with a hydrogen atom attached.

The molecules are hexagonal close-packed as shown in Fig. 2, with the layers parallel to the plane (001). The ideal hexagonal close packing of spheres (space group  $P6_3/mmc$ ) can be described in  $P2_1/c$ , a subgroup of  $P6_3/mmc$ , by the coordinates  $\frac{1}{4}, \frac{1}{12}, \frac{1}{4}$ . The axial ratio of the monoclinic cell with  $\beta=90^\circ$  is then  $a:b:c=0.5774:1:0.9428$ . The coordinates of the center of gravity of the molecule in this structure are 0.22, 0.05, 0.26 and the axial ratio is 0.5734:1:0.7762. The molecules therefore pack as oblate ellipsoids rather than spheres.

### Analysis of thermal motion

The structure appears to be well suited to an analysis of the thermal motion assuming rigid body motion of the molecules about their center of gravity (Cruickshank, 1956). The tensor  $T$  for the translational motion

Table 4. Observed and calculated structure factors

Columns are: Index H, |F\_obs|, F\_cal. \* = unobserved

Table with multiple columns containing numerical data for structure factors. The table is organized into several vertical sections, each with its own set of column headers (e.g., K=L, K=12 L=1, K=10 L=2, etc.). Each row contains a list of values corresponding to these headers, with some values marked with an asterisk to indicate they are unobserved.

Table 4 (cont.)

4	167	162-	-7	43*	2-	-4	139	133	-4	51	57	6	108	112	-1	150	164-	-4	145	151-	2	40*	15		
-4	61	51-	0	K= 9 L= 4	4	5	187	175-	5	50	48-	-6	192	192-	2	35*	11	5	50*	31	-2	71	77-		
5	281	276-	0	52	29	-5	51	57-	-5	51	32	-2	51	40-	-2	222	223-	-5	135	136-	3	35*	40-		
-5	40*	20	1	167	154-	6	50	29-	K= 11 L= 5	0	40*	32	0	140	140	-3	86	56	0	50*	44	-3	190	193-	
6	146	146-	-1	279	282	-6	73	68-	1	71	31	1	138	136-	-4	181	181	1	70	64-	-4	129	143-		
-6	41*	8-	2	98	78	-7	152	158-	-1	77	86	-1	346	332-	-4	60	51-	-1	133	137-	5	75	78		
7	36*	5-	-2	53	63	-8	48*	69	2	86	63-	2	51	47	5	35*	42	2	79	37-	-5	50*	43-		
-7	52	20	3	89	70	-8	4*	L= 5	-2	78	87-	-2	255	245-	-5	102	118	-2	60	52-	-6	71	72-		
-8	75	66-	-3	42*	4-	0	67	56-	3	70	52	3	77	91	-6	122	118	3	49*	35-	K= 6 L= 8	247-	8		
0	10*	20-	4	151	151	-1	126	124	-3	41*	3	-3	52	56-	-6	50	26-	-3	60	57-	0	261	267-		
1	168	163	5	72	72	-1	226	221	4	87	97-	4	40*	18	-7	41*	24	4	70	54	1	70	63-		
-1	156	158	-5	99	109	-2	142	134-	-4	88	95-	-4	51	42	K= 2 L= 7	-4	36*	1	-1	40*	5	267-	8		
2	121	127	6	115	114	-2	171	173	-5	41*	32	5	202	196-	0	177	163-	-5	51	48-	-2	134	138-		
-2	30*	41	-6	64	68	3	40*	7	K= 12 L= 5	-5	176	173	5	176	173	1	287	287	K= 10 L= 7	7	-2	50	32-		
3	41*	40	K= 10 L= 5	0	42*	9-	-3	245	247	0	170	177	6	50*	38-	-1	170	171-	0	81	98-	3	49*	46-	
-3	66	73-	0	104	87-	-4	40*	29	1	40*	36	-6	122	112-	2	225	231-	1	126	120	-3	41*	48		
4	221	214-	1	37*	18-	5	41*	39	-2	118	110	-7	60	79-	-2	181	176-	-1	59	52-	4	60	61-		
-4	237	243	-1	41*	11-	5	188	177	-2	118	118	0	155	171	3	40*	21-	2	39*	11-	-4	36*	1-		
5	72	49	7	52	11	-6	50	45-	1	80	70-	-1	80	70-	-3	40*	12-	-2	50*	45-	5	39*	19		
-5	119	124	-2	42	47	6	41*	12	-3	107	112	-1	85	67-	-4	398	393-	3	39*	14	-5	41*	14		
6	115	113	3	72	52-	-6	41*	12	-3	107	112	-2	96	97	5	132	148	-3	50*	37-	-6	41*	0		
-6	41*	35-	-3	63	12	7	51	62-	-4	118	145	5	2	305	296-	-5	96	99-	K= 11 L= 7	7	0	76	63-		
7	115	117	4	109	100	-7	42*	5	0	59	97-	3	71	79	6	50	60-	0	160	180-	1	70	67-		
-7	37*	32-	-4	74	23-	0	313	303	1	39*	37-	-3	140	148-	-6	41*	39-	1	60	73-	-1	49*	25		
-8	75	61	5	41*	39-	1	74	67-	-1	49*	32	4	95	75	-7	51	69-	-1	49*	36-	2	49*	38		
K= 4 L= 4	0	868	816	-6	90	98-	-1	305	293	2	40*	5	-4	83	83	K= 3 L= 7	2	69	47	-2	96	98			
1	54	37-	K= 11 L= 4	2	63	58-	2	63	58-	-2	59*	46-	5	40*	20	0	420	409-	-2	70	69	3	40*	6	
-1	32	20	0	191	188-	4	40*	50	-3	50*	86-	-5	73	60-	1	261	271-	-3	61	79-	-3	80	90		
2	480	473-	1	208	204-	3	312	317	K= 0 L= 6	6	50	58	-1	127	130-	-1	127	130-	K= 12 L= 7	7	4	49*	43-		
-2	246	245-	-1	46*	52	-3	140	144	0	120	122	-6	41*	2-	2	49*	35	0	40*	27	-4	40*	5		
3	63	64-	2	83	99-	4	40*	9-	1	167	169-	-7	41*	41	-2	151	149-	1	39*	43	-5	35*	8		
-3	74	80	-2	154	158-	-4	41*	23	-1	523	525-	K= 7 L= 6	3	86	84-	-1	35*	29	K= 8 L= 8	8	0	122	121-		
4	41*	43	3	36*	10-	5	144	146-	2	49*	48-	0	181	184	-3	139	136-	-2	61	40	0	122	121-		
-4	51	32	-3	51	32-	-5	123	133-	-2	145	135	1	41*	12-	4	10*	44-	K= 0 L= 8	8	1	60	82-			
5	182	198-	4	127	146-	6	71	70-	-3	49*	48	-1	117	111	-4	71	48-	0	70	43	-1	70	72		
-5	177	176-	-4	51	31	-6	63	12-	-3	186	180-	2	72	49	5	40*	17	1	158	150-	2	238	222-		
6	36*	23	5	41*	8-	7	88	107*	4	183	184	-2	85	71-	-5	102	103	-1	76	59-	-2	147	146-		
-6	52	38-	-5	51	53	-7	42*	5-	-4	86	69	3	81	79	6	50*	45	2	466	471-	3	39*	34		
7	51	52	K= 12 L= 4	0	132	124	K= 6 L= 5	5	36*	30	-3	52	47-	-6	41*	15	-2	244	226-	-3	40*	47			
-7	106	108-	0	77	63	0	172	175	6	41*	25-	-4	73	78	K= 4 L= 7	-7	51	61	3	136	134	4	60	81-	
-8	101	109-	K= 5 L= 4	-1	40*	22-	-1	167	160	-6	110	108	5	40*	41-	0	98	96	-3	50*	17-	-4	50*	44	
0	322	327-	2	71	65-	-2	148	150-	7	36*	6	-5	41*	13-	1	114	114	-4	71	61-	K= 9 L= 8	0	39*	8	
1	367	342-	-2	71	64-	-2	103	82	K= 0 L= 9	0	29*	9	K= 8 L= 6	0	138	140	-2	51	54-	-6	71	65			
-1	324	324-	3	50*	40	-3	605	584	4	114	97	-1	81	72	0	72	66	-3	36*	44-	0	91	91		
2	659	630-	-4	60	67	-4	149	154	5	102	112-	2	294	297	-1	262	248-	4	106	105-	0	91	91		
-2	123	110-	4	60	67	-4	149	154	-2	355	367-	-2	41*	13	-4	41*	13	-4	41*	13	1	70	43-		
3	256	239-	K= 13 L= 4	0	157	165-	-5	73	66-	-2	355	367-	-2	42*	16-	5	40*	19	-1	49*	35	-4	40*	35	
-3	53	53-	0	137	165-	-6	114	102	3	86	79-	-2	42*	16-	5	40*	19	-1	49*	35	-4	40*	35		
4	97	84-	-1	109	3-	-7	77*	18	-3	123	129	3	95	83-	-5	36*	26	2	131	127-	K= 10 L= 8	0	35*	15	
-4	162	156-	-1	216	242-	-6	77*	18	-3	123	129	3	95	83-	-5	36*	26	2	131	127-	K= 10 L= 8	0	35*	15	
5	51	35-	2	184	187-	-7	74	91	4	40*	5	-4	60	63	-4	36*	39-	-6	72	55	3	79	47		
-5	134	130-	-2	59	80-	K= 7 L= 5	0	47*	75	5	20*	66	-4	36*	39-	-6	72	55	3	79	47	0	35*	15	
6	110	106	-2	59	80-	K= 7 L= 5	0	47*	75	5	20*	66	-4	36*	39-	-6	72	55	3	79	47	0	35*	15	
-6	42*	23	-3	160	144-	1	434	424	-5	173	158	5	50*	44-	K= 5 L= 7	0	271	271-	-4	69	74	-2	39*	32-	
7	36*	36	K= 14 L= 4	-1	136	140-	6	41*	20	-6	72	67	-6	97	109	1	229	218-	-5	40*	1-	K= 11 L= 8	8		
-7	37*	38	0	39*	41	-2	84	92	-7	51	24	0	121	119	-2	157	144	6	59	44-	0	49*	26-		
-8	43*	25	0	39*	30	-3	113	120	-7	51	24	0	121	119	-2	157	144	6	59	44-	0	49*	26-		
K= 6 L= 4	0	162	150	-2	48*	30	-4	50	35	0	53	54	-2	112	97	-2	112	137	-3	164	162-	-2	49*	5-	
0	53	24	K= 1 L= 5	0	335	334	-4	117	123-	1	41*	42	-2	112	97	-2	112	137	-3	164	162-	-2	49*	5-	
-1	54	30	0	617	618	5	50	45	-1	112	99	-2	112	97	-2	112	137	-3	164	162-	-2	49*	5-		
2	42*	10	-1	50	53	-5	194	201-	-2	120	107	3	80	57-	-4	41*	3	-1	40*	23-	K= 1 L= 9	0	134	145	
-2	323	322	0	335	334	-4	117	123-	-2	41*	4	-3	103	105	5	154	140	2	49*	48-	1	28*	36-		
3	228	236-	-1	50	53	-5	194	201-	-6	73	50	-3	235	224	-4	35*	21	-5	50	59	-2	102	96		
-3	270	267	-2	169	173	-6	62	52-	-7	170	152-	-3	192	187-	-4	41*	19	6	71	86	3	110	122-		
4	97	99-	-2	174	180	-7	170	152-	K= 8 L= 5	0	52	58	5	187	178	5	71	62	-6	41*	1	-3	29*	22	
-4	37*	48	-3	49*	45-	K= 8 L= 5	0	52	58	5	187	178	5	187	178	-5	82	90	7	4	76	79	-2	146	156
5	228	220-	-3	40*	13-	1	117	124-	-1	91	89-	-5	230	239	K= 10 L= 6	0	224	218	4	35*	5	-3	99	115	
-5	160	152	-4	163	157	0	52	58	-1	91	89-	-5	230	239	K= 10 L= 6	0	224	218	4	35*	5	-3	99	115	
6	107	113	5	35*	9	-1	91	89-	-2	104	105-	6	40*	33	1	50*	49	-1	165	159	-5	60	65		
-6	107	113	5	35*	9	-1	91	89-	-2	104	105-	6	40*	33	1	50*	49	-1	165	159	-5	60			

Table 4 (cont.)

1	80	82-	1	78	69-	2	60	53-	3	34*	26	-2	10*	45-	-2	63	74	0	47*	33-	2	57	97		
-1	69	67-	-1	69	56	-2	34*	21	-3	59	41-	3	33*	35	3	48*	51	1	34*	38	-2	28*	13-		
2	39*	28-	2	35*	14-	3	39*	36-	4	38*	6-	-3	68	59	-3	115	109	-1	38*	39-	-3	20*	66-		
-2	40*	7-	-2	111	136	-3	40*	34-	-6	62	87-	4	38*	46	-4	28*	7	2	38*	0	K=	3	L=		
3	68	46-	3	76	75-	-4	40*	2-	-5	34*	26-	-4	28*	18	K=	5	L=	10	-2	59	57	0	28*	17-	
-3	49*	46	-3	35*	15-	K=	9	L=	9	1	L=	10	-5	34*	5-	0	83	65-	-3	39*	31	0	28*	37-	
4	49*	10-	4	69	82-	0	44*	74	0	38*	29	K=	3	L=	10	1	83	85	K=	8	L=	10	-1	38*	10-
-4	57	45	-4	36*	21	1	44*	52-	1	10*	12-	0	48*	25	-1	48*	36	0	47*	10-	-2	34*	20-		
-5	40*	7	-5	46*	92	-1	39*	21-	-1	28*	6-	-1	38*	25-	2	38*	27	-1	47*	25	-2	88	119-		
K=	5	L=	9	K=	7	L=	9	2	39*	12-	2	38*	37-	-1	108	94	-2	48*	30	-2	48*	26-	-3	20*	63-
0	49*	30	0	68	88	-2	49*	13	-2	74	74-	2	48*	62-	3	38*	10-	K=	1	L=	11	K=	4	L=	
1	85	101	1	39*	24	-3	35*	13-	3	38*	8	-2	91	94-	-3	28*	26	0	10*	28-	0	39*	13-		
-1	39*	20-	-1	120	123	K=	10	L=	9	-3	38*	36	3	47*	34	-4	39*	48-	1	47*	2-	-1	38*	5-	
2	58	59-	2	78	76	0	34*	35	4	38*	50-	-3	48*	3	K=	6	L=	10	-1	48*	39	-1	39*	5-	
-2	69	64	-2	85	97	-1	44*	67-	-4	20*	71	-4	59	56	0	48*	1-	2	61	91	-2	28*	21		
3	109	114-	3	40*	32	K=	0	L=	10	-5	48*	5	-5	39*	30	1	38*	12	-2	45*	8-	-3	28*	3	
-3	39*	25-	-3	60	32	0	61	65-	K=	2	L=	10	K=	4	L=	10	-1	38*	30-	-3	28*	7-	K=	5	L=
4	39*	42-	-4	87	97	1	91	110-	0	138	143	0	177	170	2	39*	24	K=	2	L=	11	0	38*	7	
-4	39*	9-	K=	8	L=	9	-1	10*	1	1	48*	18	1	103	97	-2	68	33	0	68	50	1	38*	26	
-5	40*	18	0	34*	27-	2	136	150	-1	28*	31	-1	48*	33	-3	48*	37-	1	48*	32-	-1	48*	54-		
K=	6	L=	9	1	49*	49-	-2	77	60-	2	67	50	2	38*	3-	K=	7	L=	10	-1	20*	85	-2	58	82-
0	120	135-	-1	39*	28-																				

of the mass center and the tensor  $\omega$  for the rotational motion were determined by least squares from the observed anisotropic temperature factors given in Table 2,

thus assuming that the molecules can be regarded as independent rigid bodies (Coulter, Gantzel & Trueblood, 1962).  $T$  and  $\omega$ , obtained by assuming the same

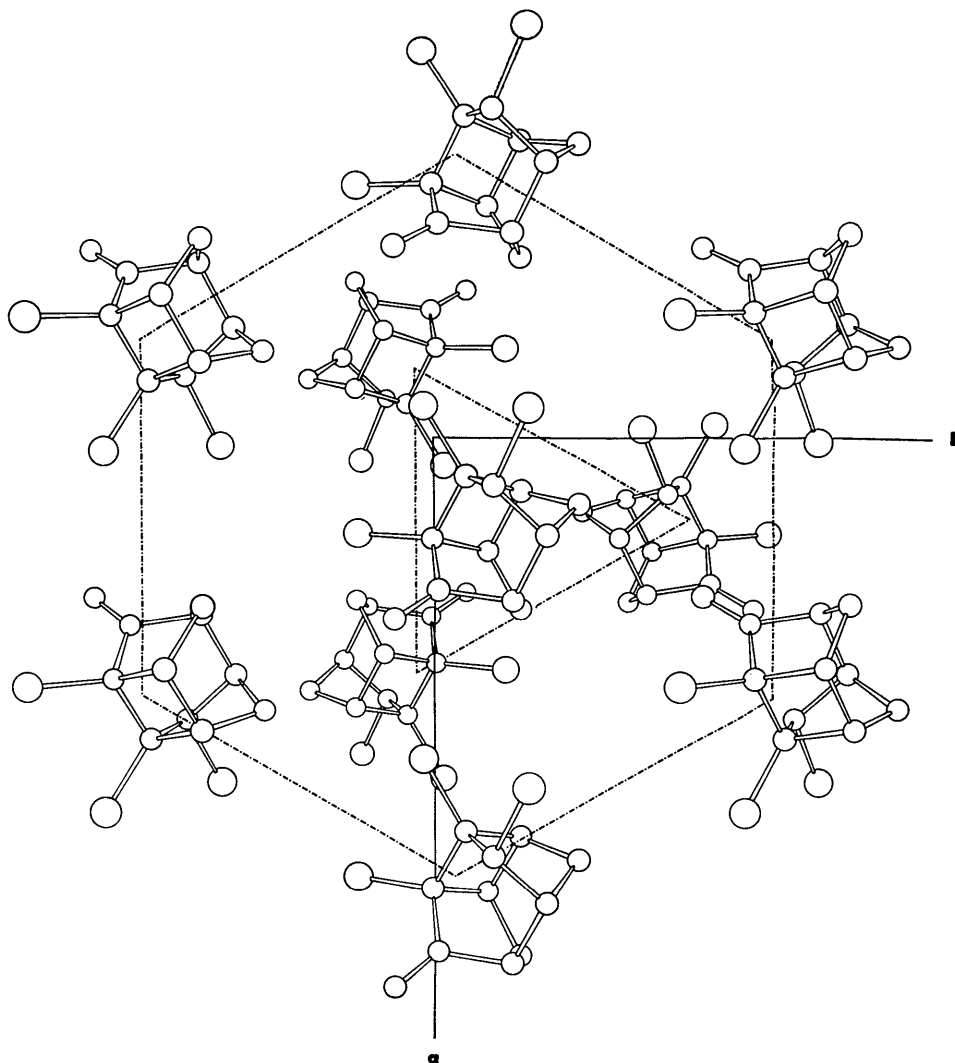


Fig. 2. Hexagonal close-packing of the molecules. The structure is viewed along  $c^*$ . The molecules at the corners and in the center of the hexagon lie in the same plane, the ones at the corners of the triangle in a different plane below. The sequence of these two planes is repeated by translation along  $c$ .

weights for all  $\beta_{ij}$ , are given in Table 7, relative to a Cartesian coordinate system with  $x||a, y||b, z||c^*$ , together with their e.s.d.'s determined by the least-squares procedure. The atomic vibration parameters  $U_{ij}$  ( $\text{\AA}^2$ ) calculated from  $T$  and  $\omega$  are given relative to the same coordinate system in Table 8, together with the observed values. The mean square atomic vibration amplitude  $u^2$  in a direction given by the direction cosines  $l_i$  is  $u^2 = \sum U_{ij}l_i l_j$ . The r.m.s. difference between  $(U_{ij})_{\text{obs}}$  and  $(U_{ij})_{\text{calc}}$  is 0.0061  $\text{\AA}^2$ , the standard deviation

of the  $(U_{ij})_{\text{obs}}$  estimated from the fit with the  $(U_{ij})_{\text{calc}}$  therefore 0.0066  $\text{\AA}^2$ . The average e.s.d. of the  $(U_{ij})_{\text{obs}}$  derived from the e.s.d.'s of the  $\beta_{ij}$  is 0.003  $\text{\AA}^2$  for C and O, 0.001  $\text{\AA}^2$  for Cl. Inspection of Table 8 therefore shows that there is a very significant difference between the  $(U_{ij})_{\text{obs}}$  and  $(U_{ij})_{\text{calc}}$  which is greatest for the Cl atoms.

The tensor components obtained by weighting the  $\beta_{ij}$  according to their e.s.d.'s (Stewart, 1966) differ from the ones in Table 7 by amounts up to  $3\sigma$ . The differ-

Table 5. Bond lengths

The estimated standard deviations given in parentheses refer to the last decimal position.

<i>i</i>	<i>j</i>	$D_{ij}$	<i>i</i>	<i>j</i>	$D_{ij}$
C(1)	C(2)	1.528 (7) $\text{\AA}$	C(1)	H(1)	1.02 (6) $\text{\AA}$
C(1)	C(6)	1.574 (8)	C(5)	H(5)	1.05 (6)
C(1)	C(10)	1.547 (9)	C(6)	H(6)	0.98 (6)
C(2)	C(3)	1.526 (7)	C(7)	H(7-1)	1.02 (7)
C(3)	C(4)	1.552 (7)	C(7)	H(7-2)	1.04 (7)
C(3)	C(9)	1.572 (7)	C(8)	H(8)	0.98 (7)
C(4)	C(5)	1.550 (7)	C(9)	H(9)	1.05 (7)
C(4)	C(8)	1.554 (7)	C(10)	H(10-1)	1.07 (7)
C(5)	C(6)	1.517 (8)	C(10)	H(10-2)	1.06 (8)
C(6)	C(7)	1.530 (8)			
C(7)	C(8)	1.527 (8)			
C(8)	C(9)	1.555 (8)			
C(9)	C(10)	1.547 (8)			
C(2)	O	1.194 (6)			
C(3)	Cl(3)	1.754 (4)			
C(4)	Cl(4)	1.753 (5)			
C(5)	Cl(5)	1.795 (6)			

Table 6. Bond angles

The estimated standard deviations given in parentheses refer to the last decimal position.

<i>i</i>	<i>j</i>	<i>k</i>	Angle ( <i>ijk</i> )	<i>i</i>	<i>j</i>	<i>k</i>	Angle ( <i>ijk</i> )
C(2)	C(1)	C(6)	108.5 (4)°	C(2)	C(1)	H(1)	107 (4)°
C(2)	C(1)	C(10)	97.2 (4)	C(6)	C(1)	H(1)	114 (4)
C(6)	C(1)	C(10)	110.7 (5)	C(10)	C(1)	H(1)	118 (4)
C(1)	C(2)	C(3)	102.9 (4)	C(4)	C(5)	H(5)	118 (4)
C(2)	C(3)	C(4)	109.8 (4)	C(6)	C(5)	H(5)	112 (4)
C(2)	C(3)	C(9)	103.9 (4)	Cl(5)	C(5)	H(5)	104 (4)
C(4)	C(3)	C(9)	89.7 (4)	C(1)	C(6)	H(6)	109 (4)
C(3)	C(4)	C(5)	107.7 (4)	C(5)	C(6)	H(6)	111 (4)
C(3)	C(4)	C(8)	90.4 (4)	C(7)	C(6)	H(6)	111 (4)
C(5)	C(4)	C(8)	105.8 (4)	C(6)	C(7)	H(7-1)	109 (4)
C(4)	C(5)	C(6)	99.9 (4)	C(8)	C(7)	H(7-1)	119 (4)
C(1)	C(6)	C(5)	108.5 (5)	C(6)	C(7)	H(7-2)	106 (4)
C(1)	C(6)	C(7)	110.5 (4)	C(8)	C(7)	H(7-2)	113 (4)
C(5)	C(6)	C(7)	102.3 (4)	H(7-1)	C(7)	H(7-2)	109 (5)
C(6)	C(7)	C(8)	100.2 (4)	C(4)	C(8)	H(8)	118 (4)
C(4)	C(8)	C(7)	105.0 (4)	C(7)	C(8)	H(8)	115 (4)
C(4)	C(8)	C(9)	90.3 (4)	C(9)	C(8)	H(8)	115 (4)
C(7)	C(8)	C(9)	110.9 (5)	C(3)	C(9)	H(9)	115 (4)
C(3)	C(9)	C(8)	89.6 (4)	C(8)	C(9)	H(9)	121 (4)
C(3)	C(9)	C(10)	103.7 (4)	C(10)	C(9)	H(9)	113 (4)
C(8)	C(9)	C(10)	111.1 (5)	C(1)	C(10)	H(10-1)	112 (4)
C(1)	C(10)	C(9)	101.1 (5)	C(9)	C(10)	H(10-1)	114 (4)
				C(1)	C(10)	H(10-2)	115 (4)
				C(9)	C(10)	H(10-2)	120 (4)
				H(10-1)	C(10)	H(10-2)	96 (5)
C(1)	C(2)	O	129.6 (5)				
C(3)	C(2)	O	127.4 (5)				
C(2)	C(3)	Cl(3)	112.9 (4)				
C(4)	C(3)	Cl(3)	118.6 (3)				
C(9)	C(3)	Cl(3)	119.2 (4)				
C(5)	C(4)	Cl(4)	115.5 (4)				
C(3)	C(4)	Cl(4)	116.6 (4)				
C(8)	C(4)	Cl(4)	117.5 (4)				
C(4)	C(5)	Cl(5)	112.4 (4)				
C(6)	C(5)	Cl(5)	111.2 (4)				

ences of the  $(U_{ij})_{\text{obs}}$  and  $(U_{ij})_{\text{calc}}$  remain about the same. They could be due to systematic errors in the  $\beta_{ij}$  or, contrary to expectation, the rigid body model is not applicable. Since a large part of the high order intensities were unobserved, the  $\beta_{ij}$  might well be biased, in which case the weighting is not meaningful. However, the results might give some qualitative information about the thermal motion of the molecule, in that the vibration tensors  $\mathbf{T}$  and  $\omega$  are both nearly isotropic, and the r.m.s. amplitudes of the translational movement and of the rotation are about 0.2 Å and 3.4°, respectively.

The atomic positions were corrected for this motion (Cruickshank, 1961) and new bond lengths and angles calculated. They differ from those given in Tables 5 and 6 and discussed above by less than  $\frac{1}{2}\sigma$ .

Table 7.  $\mathbf{T}$  and  $\omega$  tensors for rigid body motion

$\mathbf{T}$  and its estimated standard deviation is given in  $10^{-2} \text{ \AA}^2$ ,  $\omega$  in  $(^\circ)^2$ .

	11	22	33	12	13	23
$\mathbf{T}$	4.38	3.37	4.57	0.30	-0.67	0.06
e.s.d. ( $\mathbf{T}$ )	0.21	0.23	0.27	0.18	0.19	0.20
$\omega$	10.2	12.6	13.4	-0.7	-1.5	0.6
e.s.d. ( $\omega$ )	2.6	2.2	1.9	1.6	1.5	1.5

**APPENDIX**

After this paper had been submitted for publication, Dr K. N. Trueblood kindly analyzed the thermal parameters for rigid body motion using a new program by Schomaker & Trueblood (1966). Besides the tensors  $\mathbf{T}$  for translation and  $\mathbf{L}$  for libration, the program calculates an additional tensor  $\mathbf{S}$  to account for correlations between libration and translation ( $\mathbf{L}$  is the same as Cruickshank's  $\omega$ ). The results obtained were substantially better than the ones mentioned above. The e.s.d. of the  $(U_{ij})_{\text{obs}}$ , derived from the differences  $\Delta U_{ij}$  (Table 9) was found to be  $0.0037 \text{ \AA}^2$ . Thus the rigid body model now explains the observed temperature parameters quite accurately.

Table 10. Results of the analysis of thermal motion by K. N. Trueblood

Principal axes of translation tensor  $\mathbf{T}$  (Å) and libration tensor  $\mathbf{L}$  ( $^\circ$ ).

	Axes	Direction cosines to a, b, c <sup>*</sup>		
$\mathbf{T}$	0.223	-0.6126	-0.0300	0.7898
	0.195	0.7323	0.3549	0.5811
	0.182	-0.2976	0.9346	-0.1954

Table 8. Analysis of thermal parameters for rigid body motion. Observed and calculated  $U_{ij}$  (in  $10^{-2} \text{ \AA}^2$ )

	$U_{11}$		$U_{22}$		$U_{33}$		$U_{12}$		$U_{13}$		$U_{23}$	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
C(1)	4.31	4.85	4.84	5.08	5.65	6.30	-0.20	-0.41	-0.95	-1.07	0.19	-0.28
C(2)	5.14	4.63	4.96	4.70	4.60	5.73	1.00	0.74	-0.97	-1.00	-0.09	0.13
C(3)	5.54	4.71	2.90	3.65	4.96	4.89	0.56	0.48	-0.88	-0.50	-0.57	-0.06
C(4)	3.92	4.40	3.50	3.57	5.55	4.73	-0.39	0.30	-0.74	-0.72	0.85	0.05
C(5)	4.56	5.02	4.10	3.88	4.45	4.73	0.81	0.40	-0.21	-0.54	-0.27	-0.11
C(6)	4.31	5.74	4.28	3.85	5.48	5.51	-0.31	-0.09	-0.62	-0.78	-0.66	-0.48
C(7)	5.81	6.66	3.69	3.38	6.26	6.28	0.38	0.36	-0.24	-0.41	0.01	0.21
C(8)	5.99	5.51	4.39	3.85	5.00	5.02	0.23	0.54	-0.66	-0.71	0.17	0.49
C(9)	5.79	5.44	4.73	4.43	4.92	5.08	0.51	0.15	0.33	-0.01	0.45	0.30
C(10)	5.09	5.25	5.98	5.49	5.76	7.03	0.05	-0.74	0.68	0.21	0.40	0.21
O	6.80	5.79	5.73	6.02	6.15	7.01	2.28	2.78	-1.51	-1.54	0.51	0.58
Cl(3)	9.19	7.14	3.79	3.98	6.60	6.34	0.84	0.78	-0.78	-0.20	-1.22	-0.80
Cl(4)	4.96	4.81	5.04	5.41	8.43	10.23	-1.29	-0.47	-1.97	-1.08	0.03	-0.28
Cl(5)	4.75	6.20	5.14	5.79	7.97	9.47	0.55	1.19	1.02	1.29	-0.33	-0.50

Table 9.  $\Delta U_{ij} = (U_{ij})_{\text{obs}} - (U_{ij})_{\text{calc}}$ , obtained by K. N. Trueblood (in  $10^{-2} \text{ \AA}^2$ )

	$\Delta U_{11}$	$\Delta U_{22}$	$\Delta U_{33}$	$\Delta U_{12}$	$\Delta U_{13}$	$\Delta U_{23}$
C(1)	0.11	-0.24	0.13	-0.19	-0.33	0.57
C(2)	0.27	0.23	-0.44	-0.08	-0.22	-0.10
C(3)	0.12	-0.79	0.30	-0.06	-0.18	-0.41
C(4)	-0.66	0.04	0.37	-0.38	0.27	0.71
C(5)	0.09	0.37	-0.58	0.72	-0.03	-0.31
C(6)	-0.27	0.53	0.25	-0.19	-0.22	-0.23
C(7)	0.36	0.36	-0.04	0.25	0.09	-0.35
C(8)	0.55	0.49	-0.14	-0.13	0.39	-0.37
C(9)	-0.17	0.08	0.32	0.10	0.50	0.21
C(10)	0.06	0.32	-0.44	0.28	0.12	0.23
O	0.42	-0.28	-0.04	-0.02	-0.30	0.04
Cl(3)	0.17	-0.35	0.07	-0.16	0.10	-0.13
Cl(4)	-0.65	-0.20	0.01	-0.22	-0.09	0.25
Cl(5)	-0.39	-0.53	0.23	0.09	-0.10	-0.12



Table 10 (cont.)

L	4.00	0.4203	-0.8085	-0.4119
	3.59	0.1769	0.5184	-0.8366
	3.27	0.8900	0.2790	0.3606

Displacements of the libration axes from the origin (0,0,0) in Å, referred to the directions of the principal axes of L. Screw pitches of the libration axes in Å<sup>(°)</sup><sup>-1</sup>.

Axis	Displacement along axis			Screw pitch
	1	2	3	
1		-1.55	2.86	0.0043
2	-1.60		2.95	-0.0098
3	-1.15	-1.63		0.0052

The standard deviations of the r.m.s. amplitudes are 0.003 Å for T and 0.25° for L.

Table 10 describes the results in terms of three translations and three screw librations about three non-intersecting axes. Of the three screw pitches, only two are independent. The ones listed are derived by setting the trace of *S* equal to zero. *T* and *L* are not very different from the tensors listed in Table 7, and the screw pitches are quite small. However, the three libration axes do not intersect. The axes 2 and 3 are displaced by 0.45 Å parallel to axis 1.

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## The Crystal Structure of Decammine- $\mu$ -peroxo-dicobalt Pentanitrate\*

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The structure of decammine- $\mu$ -peroxo-dicobalt pentanitrate,  $(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5(\text{NO}_3)_5$ , has been re-examined. The substance forms tetragonal crystals,  $a = 11.96$ ,  $c = 8.08$  Å; there are two formula units in the cell. We have collected a completely new set of data and, working in space group  $P4_2/mmm$ , we have refined the structure to an *R* index of 0.054 for 361 non-zero reflections. Every atom in the structure, except the cobalt atoms, appears to suffer some degree of disorder; for some of the nitrate groups this disorder is so severe as to prevent a satisfactory description of them. However, the detailed structure of the cation is clear: each cobalt atom is bonded to only one of the oxygen atoms of the bridging  $-\text{O}_2-$  group, and the O-O axis is skewed to the Co-Co axis, just as was found in the salt  $(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5\text{SO}_4(\text{HSO}_4)_3$ . The O-O distance and the planarity of the Co-O-O-Co atoms both indicate that the bridging group is a superoxide radical, rather than a peroxide ion.

### Introduction

The crystal structure of decammine- $\mu$ -peroxo-dicobalt pentanitrate,  $(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5(\text{NO}_3)_5$ , was first

investigated by Vannerberg & Brosset (1963; hereafter VB). They derived a structure, based on the space group  $P4_2/m$ , in which the bridging peroxide group was perpendicular to the Co-Co direction (I); this arrangement had been proposed earlier on theoretical grounds by Vlček (1960). On the other hand, we have found a skewed arrangement (II) for the cation  $[(\text{NH}_3)_5\text{CoO}_2\text{Co}(\text{NH}_3)_5]^{5+}$  crystallized as the monosulfate tris(bisulfate) salt (Schaefer & Marsh, 1966). We

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