

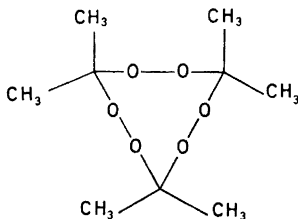
## Crystal Structure of 3,3,6,6,9,9-Hexamethyl- 1,2,4,5,7,8-hexa-oxacyclononane ("Trimeric Acetone Peroxide")

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The crystals are monoclinic with lattice parameters  $a=13.92_4$  Å,  $b=10.79_0$  Å,  $c=7.97_0$  Å, and  $\beta=91.6_4^\circ$ . The space group is  $P2_1/c$  and the cell contains four molecules. The phase problem was solved three-dimensionally by means of a computer procedure based on direct methods. Full-matrix least squares refinement gave the  $R$ -value 7.0 % for 1353 observed reflections. Rigid-body motion analysis including the  $S$ -tensor has been carried out. The molecule has approximately the symmetry  $D_3$  and the nine-membered ring may be described in terms of a "twisted boat chair". The environment of the ring carbon atoms is asymmetric; the distortion may possibly be explained by *intra*-molecular repulsions between hydrogen atoms and oxygen atoms. The O—O distance is  $1.48_3$  Å and the C—O—O angle  $107.4^\circ$ . The C—O bond length of  $1.42_2$  Å is significantly shorter than corresponding values for dimeric peroxides.

### Trimeric acetone peroxide



has been synthesized by T. Ledaal at this university by oxidation of acetone by means of hydrogen peroxide in the presence of  $\text{HClO}_4$ . The crystal structure analysis was carried out as part of a study of the stereochemical features of cyclic organic peroxides.<sup>1-4</sup>

## CRYSTAL DATA

Trimeric acetone peroxide belongs to the monoclinic system, the systematic absences leading to the space group  $P2_1/c$ . The cell parameters at room temperature obtained from  $h0l$ - and  $hk0$ -precession diagrams, and their estimated standard deviations are:

$$\begin{array}{ll} a = 13.925 \text{ \AA} & \sigma(\text{\AA}) = 0.005 \\ b = 10.790 \text{ \AA} & \sigma(\text{\AA}) = 0.004 \\ c = 7.970 \text{ \AA} & \sigma(\text{\AA}) = 0.004 \\ \beta = 91.64^\circ & \sigma(^\circ) = 0.05 \end{array}$$

The unit cell contains four molecules ( $\rho_{\text{calc}}=1.23 \text{ g.cm}^{-3}$ ,  $\rho_{\text{obs}}=1.22 \text{ g.cm}^{-3}$ ).

The intensity material was obtained from photometric measurements of integrated Weissenberg diagrams corresponding to  $hk0$ ,  $0kl \cdots 6kl$ , and  $h0l \cdots h5l$  ( $\text{CuK}\alpha$ -radiation). The diagrams were taken at room temperature, and due to instability three crystals had to be used. 1353 independent reflections were strong enough to be measured while 465 were given  $\frac{1}{4}I_{\text{min}}$ -values.

After cross-layer scaling the intensities were statistically put on absolute scale, and the overall temperature factor,  $B=2.5 \text{ \AA}^2$ , was used in the calculation of unitary structure factors, and as starting parameter in the isotropic refinement.

No corrections have been made for absorption or secondary extinction effects.

## DETERMINATION AND REFINEMENT OF THE STRUCTURE

The phase problem was solved three-dimensionally by means of a computer procedure (programmed in FORTRAN IV for CDC 3300) based on direct methods.<sup>5-7</sup> As would be expected from the  $|U|$ -distribution given in Table 1,

Table 1. Distribution of  $|U|$ -values.

Range of $ U $	Number of reflections	Range of $ U $	Number of reflections
0.00—0.01	9	0.09—0.10	101
0.01—0.02	78	0.10—0.15	398
0.02—0.03	100	0.15—0.20	215
0.03—0.04	151	0.20—0.25	116
0.04—0.05	153	0.25—0.30	40
0.05—0.06	108	0.30—0.35	19
0.06—0.07	82	0.35—0.40	10
0.07—0.08	129	0.40—0.50	4
0.08—0.09	102	0.50—1.00	3

the programmed application of Harker-Kasper inequalities gave some sign relationships; in fact, 21 signs could be expressed in terms of two unknown and three origin-fixing signs. By applying a set of linked programs,<sup>8</sup> 200 additional signs were determined in turn on basis of the four possible combinations of the two unknown, and the corresponding three-dimensional Fourier

syntheses were calculated and scanned for peaks greater than  $1 \text{ e}\cdot\text{\AA}^{-3}$ . The process was completed by a calculation of all distances less than  $2 \text{ \AA}$  between peak maxima.

Three of the sign combinations led to meaningless results, while the fourth Fourier synthesis contained 16 peaks greater than  $2.5 \text{ e}\cdot\text{\AA}^{-3}$ , 15 of which clearly showed the molecule. The 6 oxygen atoms came out with densities between 8 and  $6 \text{ e}\cdot\text{\AA}^{-3}$  while the 9 carbon atoms corresponded to peaks with heights from 2.5 to  $5 \text{ e}\cdot\text{\AA}^{-3}$ .

The  $R$ -factor corresponding to the coordinates thus obtained and the statistically determined overall temperature factor was  $R=26.1\%$  for the 500 largest structure factors. Using a program based on the minimum residual method,<sup>9</sup> this  $R$ -value was reduced to  $10.4\%$ .

A full-matrix least squares refinement<sup>8</sup> was carried out. The weighting scheme No. 1:

$$\begin{aligned} \text{for } F_o \leq \text{FB, } W &= A1(F_o)^{B1} \\ \text{for } F_o > \text{FB, } W &= A2(F_o)^{B2} \end{aligned}$$

Table 2. Fractional atomic coordinates for oxygen and carbon atoms with estimated standard deviations (multiplied by  $10^4$ ).<sup>a</sup>

Atom	$x$	$y$	$z$
O <sub>1</sub>	22669	-10233	19860
	20	24	32
O <sub>2</sub>	27980	01313	23926
	21	25	33
O <sub>3</sub>	36520	-01225	-00885
	20	25	32
O <sub>4</sub>	31035	09311	-07919
	19	25	33
O <sub>5</sub>	18152	-04437	-13038
	20	25	30
O <sub>6</sub>	13138	01565	00930
	20	23	30
C <sub>1</sub>	13251	-06924	14534
	29	34	42
C <sub>2</sub>	08744	-19237	09823
	34	39	54
C <sub>3</sub>	07805	-00002	27734
	30	44	55
C <sub>4</sub>	37115	00229	16763
	30	38	48
C <sub>5</sub>	42099	12219	21927
	35	45	61
C <sub>6</sub>	42591	-11270	22690
	36	45	61
C <sub>7</sub>	24393	04508	-20061
	32	40	45
C <sub>8</sub>	29359	-02821	-33622
	40	56	57
C <sub>9</sub>	19043	15948	-26144
	35	49	65

<sup>a</sup> For numbering of atoms, see Fig. 1.

was adapted by taking:

$$A1=10.0, A2=15.8, B1=0.0, B2=-0.5 \text{ and } FB=2.5$$

The atomic form factors used were those of Hanson *et al.*<sup>10</sup>

After 3 cycles of isotropic refinement, anisotropic thermal vibrational parameters were introduced for the oxygen and carbon atoms. 15 hydrogen atoms could be localized from a difference Fourier map while the positions of the remaining three were calculated assuming tetrahedral C—H bonds of length 1.05 Å. Reflections corresponding to  $\sin \theta/\lambda < 0.45$  were included in the refinement of hydrogen positional parameters (an attempt to refine isotropic temperature factors was unsuccessful and a constant value  $B=5.0 \text{ \AA}^2$  was used). The *R*-value arrived at for 1353 observed reflections was 7.0 %.

465 accidentally absent reflections had previously been given the value  $\frac{1}{2}I_{\min}$  and had been scaled along with the rest of the data although not used in any calculations of scale factors. Allowance for the inclusion of these reflections in the least square refinement was made by applying weighting scheme No. 3 ( $W=1/\sigma$ ). Satisfactory weight analysis was obtained by giving all

Table 3. Anisotropic thermal vibration parameters and their estimated standard deviations (multiplied by  $10^5$ ).

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O <sub>1</sub>	374	696	1414	— 66	— 98	308
	15	23	42	35	42	51
O <sub>2</sub>	384	870	1274	— 83	— 62	—175
	16	26	41	38	42	53
O <sub>3</sub>	398	835	1316	340	— 9	— 68
	16	26	44	39	44	54
O <sub>4</sub>	324	791	1444	— 73	11	44
	14	24	42	36	41	54
O <sub>5</sub>	393	827	1119	—149	— 40	15
	15	24	38	37	40	51
O <sub>6</sub>	412	672	1194	64	236	253
	16	22	40	35	42	47
C <sub>1</sub>	417	731	998	39	73	197
	22	32	47	53	55	64
C <sub>2</sub>	569	810	1685	—292	— 58	469
	27	36	67	61	74	84
C <sub>3</sub>	313	1162	1641	—113	265	96
	21	44	67	60	64	96
C <sub>4</sub>	337	856	1380	— 10	—181	—118
	21	34	59	54	61	78
C <sub>5</sub>	475	1112	2019	—216	— 68	—659
	26	47	79	67	78	105
C <sub>6</sub>	534	1103	1972	441	165	308
	28	48	79	70	81	104
C <sub>7</sub>	471	928	1071	—273	— 47	349
	24	36	51	59	59	75
C <sub>8</sub>	615	1816	1306	—201	169	— 24
	32	71	67	86	76	111
C <sub>9</sub>	421	1289	2319	—181	— 14	1504
	25	53	92	69	82	120

Table 4. Fractional coordinates (multiplied by  $10^3$ ) for hydrogen atoms. The estimated standard deviations range from 0.004 to 0.007.<sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H <sub>21</sub>	079	-243	191
H <sub>22</sub>	129	-237	024
H <sub>23</sub>	026	-170	061
H <sub>31</sub>	074	-041	385
H <sub>32</sub>	113	084	317
H <sub>33</sub>	019	021	242
H <sub>51</sub>	430	112	324
H <sub>52</sub>	485	124	146
H <sub>53</sub>	391	915	193
H <sub>61</sub>	398	-194	192
H <sub>62</sub>	420	-099	363
H <sub>63</sub>	470	-117	162
H <sub>81</sub>	333	033	-370
H <sub>82</sub>	320	-110	-279
H <sub>83</sub>	259	-066	-410
H <sub>91</sub>	159	205	-172
H <sub>92</sub>	125	131	-325
H <sub>93</sub>	226	205	-341

<sup>a</sup> Referring to Fig. 1 the hydrogen atoms H<sub>n1</sub>, H<sub>n2</sub>, H<sub>n3</sub> are bonded to C<sub>n</sub>.

unobserved reflections the same constant weight  $W=A/3$ . The *R*-factor for all data was 9.6 %.

A final difference Fourier map calculated with the observed data and with phases determined by the parameters corresponding to  $R=7.0$  % contained no positive or negative regions greater than  $0.3 \text{ e} \cdot \text{\AA}^{-3}$ .

When checking the 221 signs originally determined, no discrepancies were found.

The fractional atomic coordinates and the thermal vibration parameters arrived at are given in Tables 2, 3, and 4; the expression for the anisotropic vibrations being:

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

In Table 5 calculated structure factors are compared with the observed values (and unobserved with  $F_u = \frac{1}{2} F_o(\text{min})$ ).

#### THERMAL MOTIONS

The principal axes of the thermal vibration ellipsoids for oxygen and carbon atoms were calculated from the temperature parameters given in Table 3. Root mean square amplitudes and the corresponding *B*-values for the atomic anisotropic thermal vibration along the principal axes together with the components of these axes along the crystal axes are given in Table 6.

The thermal vibration parameters of Table 3 were applied in rigid-body analyses of translational and librational motion by (I) assuming that the axes of libration intersect at the center of gravity,<sup>11</sup> (II) assuming that the axes of libration intersect at a point,<sup>12</sup> and (III) by including the *S*-tensor in order to account for correlations of libration and translation.<sup>13</sup>









Table 5. Continued.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>u</sub>	F <sub>c</sub>	h	k	l	F <sub>u</sub>	F <sub>c</sub>
11	5	2	118	-144										
11	6	0	237	-229										
12	0	-8	50	-64										
12	0	-4	34	-17										
12	0	-2	130	-134										
12	0	0	91	-77										
12	0	2	123	-93										
12	0	4	67	-60										
12	0	6	144	-143										
12	1	-7	59	-61										
12	1	-2	75	-87										
12	1	-1	118	-114										
12	1	1	106	-91										
12	1	2	84	-81										
12	1	5	119	-117										
12	2	-5	67	-59										
12	2	-2	109	-115										
12	2	-1	90	-89										
12	2	2	146	-151										
12	2	2	43	-48										
12	2	3	30	-29										
12	2	6	89	-100										
12	3	-3	87	-56										
12	3	-2	136	-134										
12	3	-2	148	-151										
12	3	-1	79	-69										
12	3	0	46	-41										
12	3	1	158	-151										
12	3	3	102	-72										
12	3	5	88	-97										
12	4	-2	71	-79										
12	4	-1	78	-72										
12	4	0	128	-121										
12	4	1	72	-58										
12	5	0	96	-91										
12	6	0	65	-52										
13	0	0	45	-35										
13	0	0	68	-56										
13	0	-2	98	-103										
13	0	0	43	-30										
13	0	2	197	-175										
13	0	4	175	-161										
13	1	-2	71	-64										
13	1	-1	143	-125										
13	1	1	173	-160										
13	1	2	98	-99										
13	2	-4	95	-84										
13	2	-2	194	-181										
13	2	-1	89	-77										
13	2	2	125	-92										
13	3	-2	77	-64										
13	3	-1	147	-139										
13	3	0	76	-63										
13	3	2	109	-115										
13	3	4	16	-12										
13	4	-2	113	-119										
13	4	-1	91	-95										
13	4	1	79	-56										
13	6	0	41	-38										
13	7	0	40	-37										
14	0	-4	66	-61										
14	0	-2	57	-54										
14	0	0	147	-129										
14	0	2	73	-64										
14	0	4	133	-145										
14	0	6	47	-50										
14	0	6	49	-49										
14	1	0	81	-85										
14	1	5	84	-85										
14	2	0	104	-105										
14	2	2	25	-21										
14	2	4	112	-132										
14	3	-4	93	-92										
14	3	-3	90	-89										
14	3	3	67	-79										
14	4	0	53	-57										
14	6	0	67	-63										
14	7	0	89	-85										
15	0	-2	111	-106										
15	0	0	80	-76										
15	0	2	72	-82										
15	1	-1	119	-118										
15	1	0	52	-54										
15	1	1	200	-184										
15	1	3	92	-80										
15	1	5	63	-87										
15	3	0	32	-30										
15	4	0	28	-21										
15	5	0	32	-25										
16	0	-4	35	-43										
16	0	-2	49	-52										
16	0	0	101	-112										
16	0	2	35	-35										
16	0	4	67	-77										
16	1	-1	138	-125										
16	1	1	72	-67										
16	1	3	52	-42										
16	2	0	49	-63										
17	0	-2	42	-37										
17	0	0	44	-40										
17	0	0	31	-33										
17	2	0	14	-20										
17	3	0	20	-25										
17	3	0	20	-25										

Table 5. Continued.

h	k	l	F <sub>h</sub>	F <sub>c</sub>	h	k	l	F <sub>h</sub>	F <sub>c</sub>	h	k	l	F <sub>h</sub>	F <sub>c</sub>	h	k	l	F <sub>h</sub>	F <sub>c</sub>
9	1	6	28	4	10	5	-2	39	-16	12	1	6	22	-10	14	1	-4	25	48
9	2	-3	37	6	10	5	2	39	-58	12	1	7	16	-23	14	1	-3	26	19
9	2	3	38	-12	10	5	4	39	22	12	2	-4	39	-35	14	1	-2	26	-53
9	2	4	40	9	10	6	0	17	-4	12	2	-3	40	33	14	1	-1	26	25
9	2	5	40	-33	10	8	0	16	-12	12	2	1	40	53	14	1	1	28	7
9	3	-4	43	42	10	10	0	12	14	12	2	5	35	-31	14	1	2	27	-29
9	3	-1	38	-3	10	11	0	9	-19	12	3	-4	42	-26	14	2	1	38	-17
9	3	3	41	-41	11	0	-6	17	-9	12	3	4	41	-19	14	2	3	35	-7
9	4	3	38	-35	11	1	-8	26	-45	12	4	2	39	-8	14	3	-2	40	-64
9	4	4	34	57	11	1	-3	29	27	12	4	2	39	-8	14	3	-1	41	3
9	5	-6	36	10	11	1	1	26	19	12	9	0	11	7	14	3	0	41	-17
9	5	-4	39	-21	11	1	3	29	26	12	10	0	8	-40	14	3	1	40	32
9	5	1	37	-53	11	1	4	29	23	13	0	-6	14	2	14	3	2	39	-18
9	5	4	39	-39	11	1	5	28	-12	13	0	-4	18	41	14	5	0	14	-39
9	5	5	38	-23	11	1	6	25	12	13	0	6	12	21	15	0	-6	3	-13
9	8	0	18	-34	11	2	-5	39	-9	13	1	-6	21	-31	15	0	4	13	22
10	0	-2	18	-11	11	2	-3	40	-24	13	1	-5	25	-13	15	1	-5	17	24
10	0	4	19	20	11	2	-2	39	-2	13	1	-4	27	-4	15	1	-4	21	-3
10	0	8	18	-3	11	2	5	38	66	13	1	-3	28	23	15	1	-3	24	-14
10	1	-7	24	-1	11	3	-6	37	30	13	1	0	29	-14	15	1	-2	25	17
10	1	-5	28	26	11	3	0	42	-12	13	1	3	28	-22	15	1	2	24	-27
10	1	-4	29	-18	11	3	1	43	-40	13	1	4	26	-23	15	1	4	19	11
10	1	-3	28	71	11	4	-2	39	-33	13	1	5	23	-41	15	5	0	12	-16
10	1	-1	26	-29	11	5	-5	35	28	13	1	6	18	6	15	7	0	9	-13
10	1	0	26	-0	11	5	-4	36	-34	13	2	-3	39	-26	16	1	-4	16	-26
10	1	3	28	-30	11	5	-2	39	44	13	2	0	40	30	16	1	-3	20	17
10	1	6	27	4	11	5	3	39	-75	13	2	1	40	62	16	1	-2	22	11
10	2	-5	40	-11	11	5	4	37	15	13	3	1	43	47	16	1	0	23	-3
10	2	-4	40	-47	11	7	0	16	21	13	3	3	40	6	16	1	2	21	8
10	2	-2	38	8	11	8	0	15	16	13	4	-3	36	34	16	3	0	12	-23
10	2	3	39	-11	11	9	0	13	6	13	4	0	38	13	16	4	0	11	19
10	3	-6	43	-53	11	10	0	11	-3	13	4	2	37	-29	16	5	0	10	-19
10	3	0	40	-5	12	1	-6	24	-18	13	5	0	16	-11	16	6	0	7	1
10	3	5	42	15	12	1	-5	27	-9	13	6	0	12	-4	17	1	-2	16	22
10	3	6	38	11	12	1	-4	28	-57	13	6	0	9	28	17	1	-1	18	8
10	4	2	38	-28	12	1	0	29	-3	14	0	-6	11	-4	17	1	1	17	24
10	4	3	39	-18	12	1	3	29	50	14	1	-6	17	6	17	1	2	15	2
10	4	-5	37	-33	12	1	4	28	-23	14	1	-5	22	32					

The results are summarized in Tables 7, 8, and 9.

From Table 7 it may be seen that the moment of inertia about the principal axes  $I_1$  and  $I_2$  are approximately equal, thus implying rotational symmetry of the molecule.

A comparison of Tables 7, 8, and 9 shows that the *magnitudes* of the corresponding principal axes of **T** and **L** agree closely while the directions deviate considerably. The angular deviations are:

(I) compared with (III)      (II) compared with (III)

principal axis	<b>T</b>	<b>L</b>	<b>T</b>	<b>L</b>
1	57°	36°	40°	50°
2	58°	63°	60°	57°
3	44°	60°	73°	46°

The r.m.s. deviation of the observed  $U_{ij}$  from those calculated with the rigid-body parameters (corrected appropriately for the number of degrees of freedom) is significantly smaller when the **S**-tensor is included than for the two other methods of analysis.

In analysis (I) the direction of the principal libration axis corresponding to the minimum angular oscillation,  $L_3$ , is approximately parallel to  $I_3$ , the principal axis of maximum moment of inertia. This effect is less pronounced when method (II) is used and no such correlation is found in analysis (III).

The position of the origin that symmetrizes **S** (Table 9) may be compared with the center of libration arrived at in analysis (II) (Table 8). The displacement from the center of mass is in the same direction for each method of analysis, and also the magnitudes agree fairly well.

Table 6. The principal axes of the thermal vibration ellipsoids given by the components of a unit vector in fractional coordinates  $e_x$ ,  $e_y$ ,  $e_z$ ; the corresponding r.m.s. amplitudes, and the  $B$ -values.

Atom	$e_x$	$e_y$	$e_z$	$(\bar{u}^2)^{\frac{1}{2}}$ (Å)	$B$ (Å <sup>2</sup> )
O <sub>1</sub>	-0.021	0.051	0.097	0.228	4.10
	0.014	0.077	-0.065	0.190	2.86
	0.068	0.000	0.046	0.188	2.79
O <sub>2</sub>	0.011	-0.088	0.034	0.230	4.17
	-0.041	0.013	0.100	0.206	3.35
	0.058	0.025	0.068	0.187	2.75
O <sub>3</sub>	0.040	0.076	-0.016	0.242	4.61
	0.005	0.011	0.125	0.205	3.32
	0.059	-0.052	0.004	0.174	2.39
O <sub>4</sub>	-0.007	0.066	0.087	0.238	4.46
	0.018	-0.061	0.090	0.193	2.94
	0.069	0.023	-0.011	0.176	2.46
O <sub>5</sub>	-0.029	0.082	0.029	0.229	4.13
	0.055	0.044	-0.052	0.191	2.87
	0.036	-0.001	0.111	0.187	2.75
O <sub>6</sub>	0.042	0.050	0.078	0.220	3.81
	-0.051	0.066	0.004	0.194	2.97
	0.029	0.042	-0.099	0.180	2.55
C <sub>1</sub>	0.026	0.082	0.040	0.213	3.57
	-0.067	0.033	0.007	0.201	3.18
	0.003	0.029	-0.119	0.175	2.41
C <sub>2</sub>	-0.044	0.054	0.066	0.263	5.47
	0.049	0.003	0.094	0.228	4.09
	0.029	0.075	-0.051	0.192	2.91
C <sub>3</sub>	-0.007	0.092	0.011	0.263	5.46
	0.020	-0.006	0.121	0.233	4.28
	0.069	0.011	-0.031	0.168	2.24
C <sub>4</sub>	0.009	0.083	-0.054	0.227	4.08
	-0.028	0.041	0.100	0.215	3.65
	0.066	0.006	0.053	0.174	2.40
C <sub>5</sub>	0.008	-0.068	0.085	0.283	6.31
	-0.042	0.046	0.078	0.239	4.51
	0.058	0.043	0.049	0.201	3.18
C <sub>6</sub>	0.038	0.077	0.020	0.277	6.07
	-0.025	0.005	0.116	0.258	5.24
	0.056	-0.051	0.043	0.195	3.00
C <sub>7</sub>	-0.037	0.075	0.031	0.253	5.05
	0.061	0.043	0.036	0.200	3.15
	0.006	0.033	-0.116	0.178	2.51
C <sub>8</sub>	0.011	-0.092	0.002	0.329	8.55
	0.070	0.015	0.024	0.244	4.71
	0.012	0.001	-0.123	0.203	3.26
C <sub>9</sub>	-0.006	0.066	0.087	0.330	8.59
	0.045	-0.047	0.077	0.213	3.58
	0.056	0.045	-0.048	0.194	2.98

Table 7. Results of rigid-body analysis (I). The principal moments of inertia of the molecule (a.m.u. Å<sup>2</sup>), unit vectors along principal axes, I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub>, defining the molecular coordinate system, and the rigid-body tensors referred to this system.

Axis	Moment	<i>x</i>	<i>y</i>	<i>z</i>
I <sub>1</sub>	304.0	-0.0615	-0.0302	0.0471
I <sub>2</sub>	305.9	-0.0335	0.0145	-0.1109
I <sub>3</sub>	480.3	-0.0159	0.0864	0.0351

$$T = \begin{pmatrix} 373 & -6 & -20 \\ & 369 & 2 \\ & & 336 \end{pmatrix} \times 10^{-4} \text{ \AA}^2, L = \begin{pmatrix} 65 & 19 & 0 \\ & 36 & 5 \\ & & 13 \end{pmatrix} \times 10^{-4} \text{ rad.}^2$$

	Eigenvalues	r.m.s. values	I <sub>1</sub>	Direction cosines I <sub>2</sub>	I <sub>3</sub>
T	0.0382 Å <sup>2</sup>	0.195 Å	-0.5445	-0.8387	-0.0127
	0.0369 »	0.192 »	-0.7602	-0.4871	-0.4299
	0.0327 »	0.181 »	-0.3544	0.2437	-0.9028
L	0.0075 rad <sup>2</sup>	4.94°	-0.8989	-0.4188	-0.1291
	0.0028 »	3.01°	-0.4338	0.8921	0.1265
	0.0012 »	2.01°	-0.0622	-0.1697	0.9835

$$\left[ \frac{\sum (\Delta U_{ij})^2 / (n-s)}{n} \right]^{\frac{1}{2}} = 0.0060^a$$

<sup>a</sup> This is the r.m.s. deviation of the observed  $U_{ij}$  from those calculated with the rigid-body parameters (corrected appropriately for the number,  $s$ , of degrees of freedom).

Table 8. Results of rigid-body analysis (II).

$$T = \begin{pmatrix} 365 & -4 & -25 \\ & 364 & 5 \\ & & 340 \end{pmatrix} \times 10^{-4} \text{ \AA}^2, L = \begin{pmatrix} 58 & 20 & -2 \\ & 39 & 5 \\ & & 16 \end{pmatrix} \times 10^{-4} \text{ rad.}^2$$

	Eigenvalues	r.m.s. values	I <sub>1</sub>	Direction cosines I <sub>2</sub>	I <sub>3</sub>
T	0.0382 Å <sup>2</sup>	0.195 Å	0.3262	0.9438	0.0536
	0.0362 »	0.191 »	-0.7933	0.3041	-0.5274
	0.0325 »	0.180 »	0.5141	-0.1295	-0.8479
L	0.0071 rad <sup>2</sup>	4.83°	-0.8474	-0.4732	-0.2407
	0.0028 »	3.02°	-0.5274	0.7026	0.2789
	0.0013 »	2.10°	-0.0611	-0.3633	0.9297

$$\left[ \frac{\sum (\Delta U_{ij})^2 / (n-s)}{n} \right]^{\frac{1}{2}} = 0.0051$$

Center of libration:

$$x = 0.2117, y = -0.0166, z = 0.0479$$

Table 9. Results of rigid body analysis (III).

(a) In the system,  $I_1, I_2, I_3$ , defined by the principal axes of inertia.

$$\mathbf{T} = \begin{pmatrix} 369 & -9 & -5 \\ & 370 & -17 \\ & & 333 \end{pmatrix} \times 10^{-2} \text{ \AA}^2, \quad \mathbf{L} = \begin{pmatrix} 63 & 14 & 0 \\ & 40 & 2 \\ & & 14 \end{pmatrix} \times 10^{-4} \text{ rad.}^2$$

	Eigenvalues	r.m.s. values	$I_1$	Direction cosines $I_2$	$I_3$
<b>T</b>	0.0379 $\text{\AA}^2$	0.195 $\text{\AA}$	-0.1539	-0.8987	-0.4107
	0.0366 »	0.191 »	-0.9866	0.1619	0.0154
	0.0324 »	0.180 »	0.0527	0.4077	-0.9116
<b>L</b>	0.0070 $\text{rad.}^2$	4.78°	-0.9463	-0.2615	0.1902
	0.0034 »	3.36°	-0.0910	0.7798	0.6296
	0.0013 »	2.09°	-0.3102	0.5689	-0.7617

$$[\sum_n (\Delta U_{ij})^2 / (n-s)]^{\frac{1}{2}} = 0.0035$$

(b) In the system,  $L_1, L_2, L_3$ , defined by the principal axes of the libration tensor  $\mathbf{L}$ .  
Symmetrizing origin:

$$\varrho_1 = -0.33 \text{ \AA}, \quad \varrho_2 = 0.13 \text{ \AA}, \quad \varrho_3 = -0.12 \text{ \AA}$$

Displacements of libration axes ( ${}^i\varrho_i$  means shift of  $L_j$  along  $L_i$ ):

$$\begin{matrix} {}^2\varrho_1 = 0.02 \text{ \AA} & {}^1\varrho_2 = 0.25 \text{ \AA} & {}^1\varrho_3 = 0.15 \text{ \AA} \\ {}^3\varrho_1 = -1.24 \text{ \AA} & {}^3\varrho_2 = -0.50 \text{ \AA} & {}^2\varrho_3 = -0.67 \text{ \AA} \end{matrix}$$

$$\mathbf{L} = \begin{pmatrix} 70 & 0 & 0 \\ & 34 & 0 \\ & & 13 \end{pmatrix} \times 10^{-4} \text{ rad.}^2, \quad \mathbf{S} = \begin{pmatrix} 207 & 1884 & -836 \\ & -723 & 1209 \\ & & 515 \end{pmatrix} \times 10^{-8} \text{ rad.} \cdot \text{\AA}$$

( $\mathbf{S}$  is reduced to new origin and symmetrized).Screw pitches ( $\sigma_i = S_{ii}/L_{ii}$  is parallel to  $L_i$ )

$$\sigma_1 = 0.030 \text{ \AA/rad.}, \quad \sigma_2 = -0.211 \text{ \AA/rad.}, \quad \sigma_3 = 0.388 \text{ \AA/rad.}$$

Effective screw translations ( $\sigma_i(L_{ii})^{\frac{1}{2}}$  is parallel to  $L_i$ )

$$\sigma_1(L_{11})^{\frac{1}{2}} = 0.002 \text{ \AA}, \quad \sigma_2(L_{22})^{\frac{1}{2}} = -0.012 \text{ \AA}, \quad \sigma_3(L_{33})^{\frac{1}{2}} = 0.014 \text{ \AA}$$

(c) In the orthogonal system,  $J_1, J_2, J_3$ , defined by  $J_1||a, J_2||b, J_3||c^*$ 

	Eigenvalues	r.m.s. values	$J_1$	Direction cosines $J_2$	$J_3$
<b>T</b>	0.0364 $\text{\AA}^2$	0.191 $\text{\AA}$	-0.3723	-0.1733	-0.9118
	0.0341 »	0.185 »	-0.8128	-0.4135	0.4104
	0.0319 »	0.179 »	-0.4481	0.8939	0.0130
<b>L</b>	0.0070 $\text{\AA}^2$	4.78°	0.9777	0.2084	0.0267
	0.0034 »	3.36°	0.0569	-0.3852	0.9211
	0.0013 »	2.09°	0.2022	-0.8990	-0.3884

 $\mathbf{T}$  is the *reduced* translation tensor(d) In the  $x, y, z$  system, *i.e.* in fractions of  $a, b, c$ .

Start origin (center of gravity)

$$x = 0.2492, \quad y = -0.0072, \quad z = 0.0377$$

Symmetrizing origin

$$x = 0.2249, \quad y = -0.0082, \quad z = 0.0575$$

Table 9 shows that the *effective translation*, defined as the screw pitch,  $\sigma_i$ , multiplied with the r.m.s. amplitude of libration about the axis  $L_i$ , is small in the direction of the axis corresponding to the largest angular oscillation. The corrections in fractional coordinates for librational effects<sup>14</sup> may be found in Table 10, which shows that all corrections are less than three times the corresponding standard deviation of the coordinate.

Table 10. Corrections in fractional atomic coordinates due to libration compared with estimated standard deviations of the coordinates. (The  $\Delta$ 's and  $\sigma$ 's are multiplied by  $10^6$ ).

Atom	$\Delta x$	$\sigma(x)$	$\Delta y$	$\sigma(y)$	$\Delta z$	$\sigma(z)$
O <sub>1</sub>	3	20	43	24	64	32
O <sub>2</sub>	10	21	10	25	77	33
O <sub>3</sub>	32	20	-5	25	-31	32
O <sub>4</sub>	18	19	50	25	-59	33
O <sub>5</sub>	-4	20	-11	25	-73	30
O <sub>6</sub>	-19	20	20	23	-13	30
C <sub>1</sub>	-18	29	-22	34	45	42
C <sub>2</sub>	-23	34	-80	39	29	54
C <sub>3</sub>	-33	30	13	44	102	55
C <sub>4</sub>	31	30	1	38	43	48
C <sub>5</sub>	38	35	57	45	60	61
C <sub>6</sub>	46	36	-58	45	66	61
C <sub>7</sub>	7	32	30	40	-106	45
C <sub>8</sub>	22	40	-7	56	-165	57
C <sub>9</sub>	-7	35	89	49	-131	65

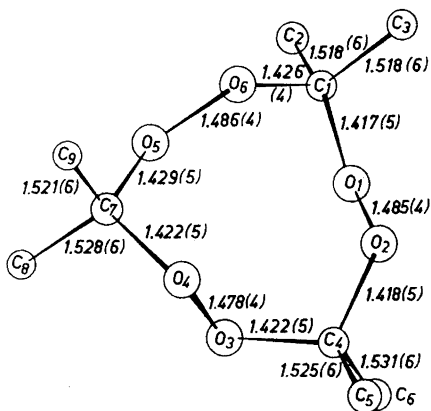


Fig. 1. Schematical drawing of the molecule showing interatomic distances.

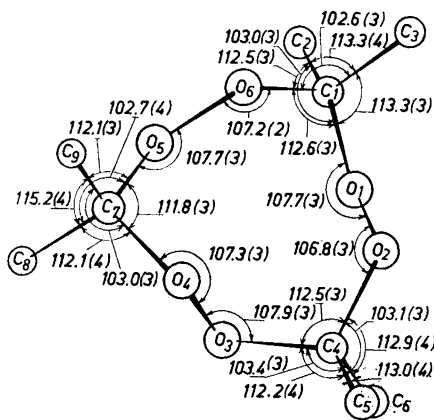


Fig. 2. Schematical drawing of the molecule showing bond angles.

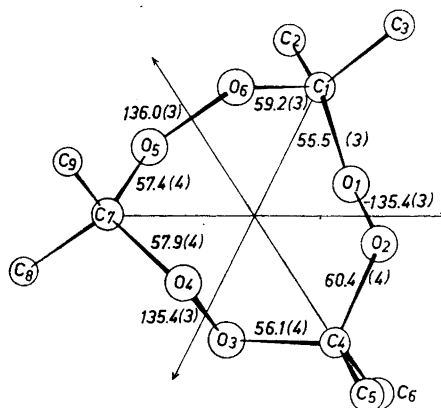
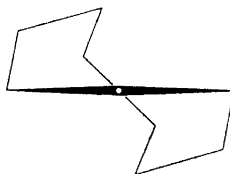


Fig. 3. Schematical drawing of the molecule showing dihedral angles. The approximate two-fold axes of symmetry are indicated.

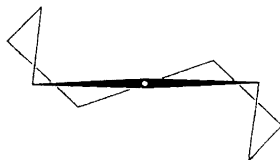
### DISCUSSION

Interatomic distances and angles (corrected for librational effects) may be found in Figs. 1 and 2 while the dihedral angles are shown in Fig. 3. The standard deviations, given in parentheses, have been calculated from the correlation matrix corresponding to the last full-matrix least squares refinement cycle without taking into account the E.S.D.'s of the cell parameters. In all figures and tables the standard deviations of distances and angles have been multiplied by  $10^3$  and 10, respectively. The largest correction for libration in distances and angles are  $1.5 \times \sigma_d$  and  $0.8 \times \sigma_a$ , where  $\sigma_d$  and  $\sigma_a$  are the corresponding standard deviations. The C—H distances arrived at range from 0.83 Å to 1.08 Å with estimated standard deviations of about 0.06 Å.

The only crystal structure analysis reported of a saturated nine-membered ring is that of cyclononylammonium bromide<sup>15</sup> where the conformation of the ring skeleton roughly may be described in terms of a twisted chair boat, TCB,<sup>16</sup> with a two-fold axis of symmetry:



The conformation of the nine-membered ring of trimeric acetone peroxide corresponds closely to the twisted boat chair, TBC,<sup>16</sup> with symmetry  $D_3$ :



The approximate three-fold symmetry of the whole molecule is confirmed by the distances and angles listed in Table 11. A unit vector,  $\mathbf{n}_3$ , along the three-fold axis of rotation is given by

$$\mathbf{n}_3 = -0.016 \cdot \mathbf{a} + 0.086 \cdot \mathbf{b} + 0.035 \cdot \mathbf{c}$$

Table 11. Distances and angles (with estimated standard deviations in parentheses) between approximately three-fold symmetry related atoms.

Distance	(Å)	Angle	(°)
O <sub>1</sub> -O <sub>2</sub>	2.762 (4)	O <sub>1</sub> -O <sub>3</sub> -O <sub>5</sub>	60.3 (1)
O <sub>1</sub> -O <sub>5</sub>	2.763 (4)	O <sub>3</sub> -O <sub>5</sub> -O <sub>1</sub>	60.3 (1)
O <sub>3</sub> -O <sub>5</sub>	2.737 (4)	O <sub>5</sub> -O <sub>1</sub> -O <sub>3</sub>	59.4 (1)
O <sub>2</sub> -O <sub>4</sub>	2.738 (4)	O <sub>2</sub> -O <sub>4</sub> -O <sub>6</sub>	60.0 (1)
O <sub>2</sub> -O <sub>6</sub>	2.731 (4)	O <sub>4</sub> -O <sub>6</sub> -O <sub>2</sub>	60.0 (1)
O <sub>4</sub> -O <sub>6</sub>	2.746 (4)	O <sub>6</sub> -O <sub>2</sub> -O <sub>4</sub>	60.3 (1)
C <sub>1</sub> -C <sub>4</sub>	3.418 (6)	C <sub>1</sub> -C <sub>4</sub> -C <sub>7</sub>	60.4 (1)
C <sub>1</sub> -C <sub>7</sub>	3.445 (5)	C <sub>4</sub> -C <sub>7</sub> -C <sub>1</sub>	59.6 (1)
C <sub>4</sub> -C <sub>7</sub>	3.429 (6)	C <sub>7</sub> -C <sub>1</sub> -C <sub>4</sub>	59.9 (1)
C <sub>2</sub> -C <sub>6</sub>	4.881 (7)	C <sub>2</sub> -C <sub>6</sub> -C <sub>8</sub>	60.2 (1)
C <sub>2</sub> -C <sub>8</sub>	4.909 (6)	C <sub>6</sub> -C <sub>8</sub> -C <sub>2</sub>	59.6 (1)
C <sub>6</sub> -C <sub>8</sub>	4.908 (7)	C <sub>8</sub> -C <sub>2</sub> -C <sub>6</sub>	60.2 (1)
C <sub>3</sub> -C <sub>5</sub>	4.998 (6)	C <sub>3</sub> -C <sub>5</sub> -C <sub>9</sub>	59.5 (1)
C <sub>3</sub> -C <sub>9</sub>	4.943 (7)	C <sub>5</sub> -C <sub>9</sub> -C <sub>3</sub>	60.6 (1)
C <sub>5</sub> -C <sub>9</sub>	4.961 (7)	C <sub>9</sub> -C <sub>3</sub> -C <sub>5</sub>	59.9 (1)

A least squares plane defined by the carbon and oxygen atoms gives the following fit:

Atoms defining the plane	Deviations (Å)	Atoms defining the plane	Deviations (Å)
C <sub>1</sub>	-0.005	O <sub>5</sub>	-0.543
C <sub>4</sub>	0.002	O <sub>6</sub>	0.545
C <sub>7</sub>	-0.001	C <sub>2</sub>	-1.212
O <sub>1</sub>	-0.520	C <sub>3</sub>	1.173
O <sub>2</sub>	0.570	C <sub>5</sub>	1.173
O <sub>3</sub>	-0.530	C <sub>6</sub>	-1.200
O <sub>4</sub>	0.550	C <sub>8</sub>	-1.212
		C <sub>9</sub>	1.188

Within probable limits of error, C<sub>1</sub>, C<sub>4</sub>, and C<sub>7</sub> are in the plane, while the atoms O<sub>1</sub>, O<sub>3</sub>, O<sub>5</sub>, C<sub>2</sub>, C<sub>6</sub>, C<sub>8</sub>, respectively, are situated approximately as far below the plane as O<sub>2</sub>, O<sub>4</sub>, O<sub>6</sub>, C<sub>3</sub>, C<sub>5</sub>, C<sub>9</sub> are above it. This fact, together with the distances given in Table 12, implies that the molecule has the three approximate two-fold axes of symmetry indicated in Fig. 3. The total symmetry of the molecule is accordingly close to  $D_3$ .



Table 12. Distances (with estimated standard deviations in parentheses) between approximately two-fold symmetry related atoms.

Distance	(Å)	Distance	(Å)	Distance	(Å)
C <sub>1</sub> -O <sub>2</sub>	2.344 (4)	C <sub>4</sub> -O <sub>4</sub>	2.345 (5)	C <sub>7</sub> -O <sub>6</sub>	2.354 (5)
C <sub>1</sub> -O <sub>5</sub>	2.345 (4)	C <sub>4</sub> -O <sub>1</sub>	2.332 (5)	C <sub>7</sub> -O <sub>3</sub>	2.336 (5)
C <sub>1</sub> -C <sub>5</sub>	4.551 (6)	C <sub>4</sub> -C <sub>9</sub>	4.535 (6)	C <sub>7</sub> -C <sub>3</sub>	4.554 (6)
C <sub>1</sub> -C <sub>8</sub>	4.539 (6)	C <sub>4</sub> -C <sub>2</sub>	4.505 (6)	C <sub>7</sub> -C <sub>8</sub>	4.538 (6)
C <sub>1</sub> -C <sub>6</sub>	4.155 (6)	C <sub>4</sub> -C <sub>8</sub>	4.159 (6)	C <sub>7</sub> -C <sub>2</sub>	4.172 (6)
C <sub>1</sub> -C <sub>9</sub>	4.189 (7)	C <sub>4</sub> -C <sub>3</sub>	4.208 (6)	C <sub>7</sub> -C <sub>5</sub>	4.198 (6)
C <sub>1</sub> -O <sub>3</sub>	3.560 (5)	C <sub>4</sub> -O <sub>5</sub>	3.547 (5)	C <sub>7</sub> -O <sub>1</sub>	3.587 (4)
C <sub>1</sub> -O <sub>4</sub>	3.569 (5)	C <sub>4</sub> -O <sub>6</sub>	3.547 (5)	C <sub>7</sub> -O <sub>2</sub>	3.559 (5)

From Figs. 1 and 2 it may be seen that, within error limits, the independent C—C, C—O, and O—O distances as well as the angles C—O—O and O—C—O, respectively, are equal. Their mean values are compared with earlier findings<sup>1-3</sup> in Table 13, where standard deviations have been calculated by regarding the

Table 13. Mean values of interatomic distances (Å) and angles (°) compared with earlier findings. Estimated standard deviations are given in parentheses.

Distance/angle	Dimeric cyclohexanone peroxide	Dimeric cycloheptanone peroxide	Dimeric cyclooctanone peroxide	Trimeric acetone peroxide
C—C	1.526 (3)	1.536 (5)	1.523 (2)	1.524 (3)
C—O	1.440 (2)	1.441 (3)	1.446 (1)	1.422 (2)
O—O	1.482 (2)	1.472 (3)	1.474 (2)	1.483 (2)
C—O—O	107.3 (1)	107.9 (1)	108.1 (1)	107.4 (1)
O—C—O	108.2 (2)	108.9 (3)	107.3 (1)	112.3 (2)
C—C—O	104.9 (1)	103.2 (2)	103.6 (1)	103.0 (1)
C—C—O	112.7 (3)	112.1 (2)	111.7 (1)	112.5 (2)

individual distances and angles as independently determined. The significantly shorter C—O bond length of the present compound may possibly be related to the fact that the O—C—O angle is opened by more than 4° compared to the dimeric peroxides.

The arrangements around the carbon atoms C<sub>1</sub>, C<sub>4</sub>, and C<sub>7</sub> are all asymmetric in a fashion which is illustrated in Fig. 4. Neither the six large nor the six small C—C—O angles are significantly different (Fig. 2), and the mean values are compared with those of the dimeric peroxides in Table 13. It should be pointed out, however, that in the present structure the C<sub>A</sub>—C<sub>R</sub>—C<sub>B</sub> groups are rotated *ca.* 6.5° about the approximate two-fold axes, which are *in* the C<sub>A</sub>—C<sub>R</sub>—C<sub>B</sub> planes, while for the dimeric peroxides

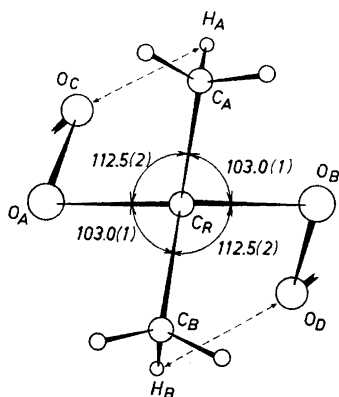


Fig. 4. Schematic drawing of a part of the molecule viewed along the approximate two-fold axis of symmetry, showing the asymmetric environment of the  $C_R$ -atoms.

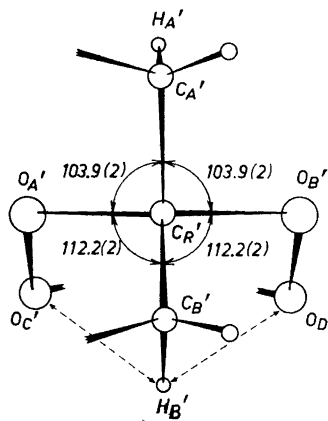


Fig. 3. Schematic drawing showing the asymmetric environment of the spiro carbon atoms of dimeric peroxides.

the rotation is about an axis, through  $C_{R'}$  normal to the  $C_{A'}-C_{R'}-C_{B'}$  plane as indicated in Fig. 5. The angles between the three pairs of  $O_A-C_R-O_B$  and  $C_A-C_R-C_B$  planes are  $96.9^\circ$ ,  $96.4^\circ$ , and  $96.4^\circ$  for  $R=1,4$ , and 7, respectively.

It seems reasonable to relate the effect to *intra*-molecular oxygen-hydrogen repulsions; between  $O_C$  and  $H_A$  (Fig. 4), and between  $O_D$  and  $H_B$ . A calculation of these (equal) distances in an undistorted model with staggered conformations of the methyl groups gives an O—H distance of about 2.4 Å; the sum of the van der Waals radii of oxygen and hydrogen being *ca.* 2.6 Å. The corresponding distances in the dimeric peroxides are even somewhat shorter.

Unfortunately, the determination of hydrogen atom positions in this structure is very poor, and no statements concerning the extent to which the distortions influence the O—H contacts can be made with confidence.

The shortest *inter*-molecular O—H and H—H contacts are 2.67 Å and 2.37 Å, respectively.

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