

## Crystal Structure of 3,6-Spiro-dicycloheptylidene-1,2,4,5-tetraoxacyclohexane ("Dimeric Cycloheptanone Peroxide")

P. GROTH

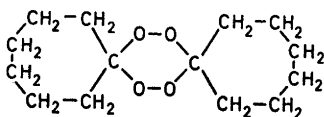
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The crystals belong to the monoclinic system with space group  $P2_1/c$ . The unit cell, containing two molecules, has the following parameters:

$$\begin{aligned} a &= 9.39, \text{ \AA} \\ b &= 6.39, \text{ \AA} \\ c &= 11.68, \text{ \AA} \end{aligned} \qquad \beta = 102.3^\circ$$

The phase problem was solved by a computer procedure based on direct methods. Full matrix least squares refinement gave the  $R$ -value 7.4 % when the 842 observed reflections were included. The O—O distance is found to be 1.47<sub>2</sub> Å and the C—O bond lengths are 1.44<sub>2</sub> Å and 1.43<sub>2</sub> Å, respectively. The environment of the spiro carbon atom is asymmetric; the distortion may possibly be explained by *intra*-molecular repulsions of hydrogen atoms from oxygen atoms. The conformation of the cycloheptylidene ring corresponds to a chair form, the average value of the C—C—C angles being 115.3°.

### Dimeric cycloheptanone peroxide



has been synthesized by T. Ledaal at this university.<sup>1</sup> The present structure analysis was carried out as part of a study of the stereochemical features of cyclic organic peroxides,<sup>2</sup> and also, in view of the problems concerning the conformations of seven-membered rings,<sup>3,4</sup> with the intention of obtaining precise information about the molecular geometry of the cycloheptylidene ring.

### CRYSTAL DATA

Dimeric cycloheptanone peroxide belongs to the monoclinic system, and the systematic absences lead to the space group  $P2_1/c$ . The cell parameters were determined by measuring 51  $2\theta$ -values on  $hk0$  and  $h0l$  Weissenberg

diagrams which were taken with unfiltered Cu-radiation, and calibrated by superimposed powder diagrams of BaF<sub>2</sub> ( $a = 6.2001 \text{ \AA}$ ). With the wavelengths for CuK $\alpha$ -radiation taken as  $\bar{\alpha} = 1.54178$ ,  $\alpha_1 = 1.54051$ ,  $\alpha_2 = 1.54433$ , and  $\beta = 1.39217 \text{ \AA}$ , least squares refinement of the lattice parameters (programmed by R. A. Sparks at UCLA) gave the following results:

$$\begin{array}{ll} a = 9.399 \text{ \AA} & \sigma (\text{\AA}) = 0.002 \\ b = 6.396 \text{ \AA} & \sigma (\text{\AA}) = 0.001 \\ c = 11.682 \text{ \AA} & \sigma (\text{\AA}) = 0.002 \\ \beta = 102.39^\circ & \sigma (^\circ) = 0.02 \end{array}$$

With two molecules in the unit cell the calculated density,  $\rho_c = 1.24 \text{ g.cm}^{-3}$ , corresponds closely to the density measured by flotation,  $\rho_0 = 1.25 \text{ g.cm}^{-3}$ .

The intensity material was obtained from photometric measurements of integrated Weissenberg diagrams corresponding to  $hk0$ ,  $h0l$ ,  $h1l$ , ...,  $h5l$  (CuK $\alpha$ -radiation). 842 reflections were strong enough to be measured while 246 accidentally absent reflections were given the value  $\frac{1}{4}I_{\min}$ , where  $I_{\min}$  is the smallest observable intensity.

The intensities were statistically put on an absolute scale, and the overall temperature factor thus obtained,  $B = 3.98 \text{ \AA}^2$ , was used in the calculation of unitary structure factors, and also as starting parameter in the isotropic least squares refinement.

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

#### DETERMINATION OF THE STRUCTURE

The phase problem was solved by direct methods using a sign determining computer procedure based on the Cochran and Douglas method,<sup>5</sup> the zero-check,<sup>6</sup> and the statistical equivalent of Sayre's equation.<sup>7</sup> The set of programmes, handling two-dimensional data only, has been written in the SPS-language for IBM-1620 by the author.

The sign determination was carried out for the  $h0l$ - and  $hk0$ -projections. The corresponding  $|U|$ -distributions are listed in Table 1.

Table 1.  $|U|$ -Distributions of the  $hk0$ - and  $h0l$ -projections.

Range of $ U $	Number of reflections	
	$hk0$ -projection	$h0l$ -projection
0.00—0.01	1	2
0.01—0.02	3	1
0.02—0.03	3	11
0.03—0.04	2	1
0.04—0.05	5	4
0.05—0.10	13	24
0.10—0.15	11	24
0.15—0.20	10	23
0.20—0.25	4	12
0.25—0.30	3	13
0.30—0.35	0	9
0.35—0.40	0	3
0.40—0.50	0	5
0.50—1.00	0	2

Starting with the  $h0l$ -projection the origin was specified by giving positive signs to the unitary structure factors  $U(101)$  and  $U(401)$  which have absolute values 0.43 and 0.28. 14 additional large  $U$ -values were selected for permutation, the resulting number of terms in the expression

$$\chi = \sum_{\mathbf{h}} \sum_{\mathbf{h}'} U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h}+\mathbf{h}'} \quad (1)$$

was 19.

32 "small" unitary structure factors ( $|U| \leq 0.06$ ) could be found for the zero-check, the corresponding number of products in the sums

$$\psi_0 = \sum_{\mathbf{k}} \left| \sum_{\mathbf{h}} U_{\mathbf{h}} \cdot U_{\mathbf{h}+\mathbf{k}} \right| \quad (2)$$

being 43.  $\chi_e$  given by

$$\chi_e = \sum_{\mathbf{h}} \sum_{\mathbf{h}'} |U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h}+\mathbf{h}'}| \cdot \tanh(N \cdot |U_{\mathbf{h}} \cdot U_{\mathbf{h}'} \cdot U_{\mathbf{h}+\mathbf{h}'}|) \quad (3)$$

where  $N$  is the number of equal atoms in the cell, was calculated, and found to be  $\chi_e = 0.396$ .

Among the  $2^{14} = 16\,384$  possible sign combinations which were tested by the programme, 12 satisfied  $\chi > \chi_e$ . The corresponding values of  $\chi$  and  $\psi_0$  are listed in Table 2. Set numbers 5 and 10, being favoured by the  $\chi$ -criterion, have also the largest  $\psi_0$ -value and were therefore regarded as less probable than the sets 4 and 12 corresponding to the smallest  $\psi_0$  and a medium  $\chi$ -value. Further, since sign set 4 only contains two negative signs, number 12

Table 2. Most probable signset for the  $h0l$ -projection.

Signset number	$\chi$	$\psi_0$
1	0.417	0.192
2	0.405	0.200
3	0.401	0.191
4	0.407	0.184
5	0.435	0.200
6	0.399	0.195
7	0.401	0.191
8	0.417	0.192
9	0.405	0.200
10	0.435	0.200
11	0.399	0.195
12	0.407	0.184

Table 3. Most probable signsets for the  $hk0$ -projection.

Signset number	$\chi$	$\psi_0$
1	0.274	0.866
2	0.278	0.520
3	0.300	0.546
4	0.352	0.494
5	0.288	0.532
6	0.292	0.418

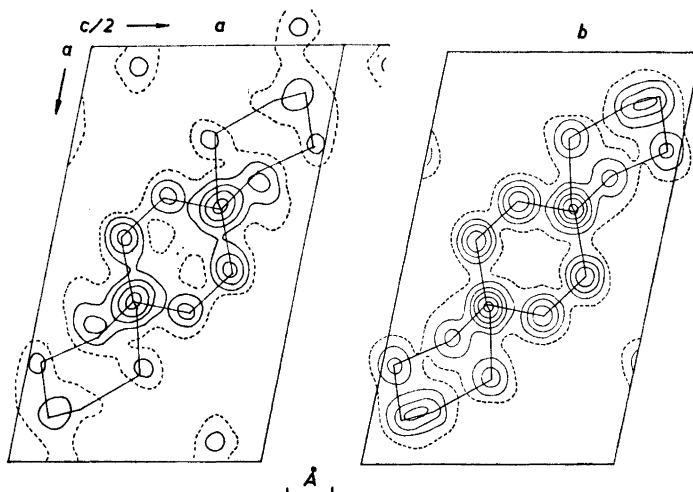


Fig. 1. Fourier projection along  $b$ -axis. (a) Calculated with the 48 "most probable" signs, (b) final map.

was selected as the "most probable" and used as basis for determination of 32 additional signs of large and moderate unitary structure factors by the relationship

$$S(U_k) = S\left(\sum_h U_h \cdot U_{h+k}\right) \quad (4)$$

where  $S$  means "sign of". In this last process the signs are redetermined until no further signshifts occur from one cycle to the next.

The 48 signs thus obtained were used in calculating the electron-density map which is reproduced in Fig. 1a compared with the final map in Fig. 1b.

The trial parameters derived from Fig. 1a corresponded to  $R_{h0l} = 39.2\%$ . Using a programme based upon the "minimum residual method"<sup>8</sup> the  $R$ -factor was reduced to 11.2%. Two cycles of isotropic least squares refinement reduced it further to 10.0%.

Comparison of the signs determined with those corresponding to  $R_{h0l} = 10.0\%$  showed no discrepancies for set number 12 of Table 2 while 6 signs had been obtained incorrectly by the application of sign relationship (4).

The method was then applied to the  $hk0$ -projection.  $U(100) = 0.21$  and  $U(110) = 0.19$  were given positive signs in order to specify the origin. With 14  $U$ 's for permutation, the sums in the  $\chi$ -expression (1) contained 51 terms, and with 9 "small"  $U$ -values ( $|U| \leq 0.04$ ) 38 products in the  $\psi_0$ -expression (2) resulted.

6 of the  $2^{14}$  possible sign combinations satisfied  $\chi > \chi_c = 0.272$ , and the corresponding  $\chi$ - and  $\psi_0$ -values are listed in Table 3. Numbers 4 and 6 are indicated as most probable, and both sets were used as basis for evaluation of 16 additional signs. With the signs evaluated from set number 4 a Fourier map was obtained which is very similar to the final map reproduced in Fig. 2.

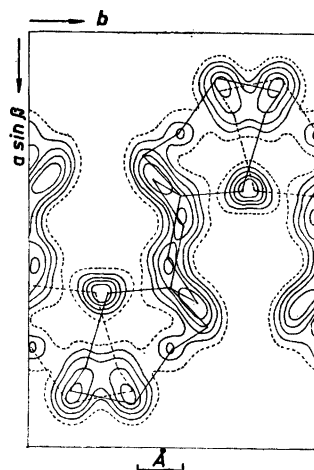


Fig. 2. Fourier projection along  $c$ -axis.

The  $R$ -value arrived at for this projection was  $R_{hko} = 12.1\%$ , and it turned out that all the 32 signs had been determined correctly.

#### REFINEMENT OF THE STRUCTURE

With the final coordinates from the two-dimensional analysis and the statistically determined overall  $B$ -value as starting parameters, a three-dimensional full-matrix least squares refinement was carried out using a programme written by Gantzel, Sparks and Trueblood<sup>9</sup> (revised for UNIVAC 1107 by cand. real. Christian Rømming at this university). The weighting scheme No. 1 was adapted by taking  $A1 = 10.0$ ,  $A2 = 14.0$ ,  $B1 = 0.0$ ,  $B2 = -0.5$ , and  $FB = 2.0$ , and the form factors calculated by Hanson, Herman, Lea, and Skillman<sup>10</sup> were used.

After 4 cycles of isotropic refinement anisotropic temperature factors were introduced for the oxygen and carbon atoms. The hydrogen atom positions had been calculated assuming tetrahedral C—H bonds of lengths  $1.05 \text{ \AA}$ , and reflections corresponding to  $\sin \theta/\lambda < 0.45$  were included in the refinement of these atoms. The  $R$ -value arrived at for the 842 observed reflections was  $7.4\%$ .

As mentioned before, 246 accidentally absent reflections had previously been given the value  $\frac{1}{4}I_{\min}$ . These reflections had also been scaled along with the rest of the data although not used in any calculations of the scale factors. Allowance for the inclusion of these reflections in the least squares refinement was made by applying weighting scheme No. 3 ( $W = 1/\sigma$ ). Satisfactory weight analysis<sup>11</sup> was obtained by giving all unobserved reflections the same constant weight  $W = A1/3$ .

With the inclusion of 246 of the accidental absences it would be roughly expected that the standard deviations (estimated from the inverse matrix of the normal equations) would decrease by a factor  $(842/(842 + 246))^{\frac{1}{2}} = 0.88$ .

**Table 4.** Fractional atomic coordinates for oxygen and carbon atoms.<sup>a</sup> (Estimated standard deviations in parantheses).

	<i>x</i>	<i>y</i>	<i>z</i>
O <sub>1</sub>	0.4587 (0.0003)	0.0330 (0.0005)	0.3818 (0.0002)
O <sub>2</sub>	0.6387 (0.0002)	0.0652 (0.0005)	0.5512 (0.0002)
C <sub>1</sub>	0.6062 (0.0004)	-0.0221 (0.0007)	0.4355 (0.0003)
C <sub>2</sub>	0.6981 (0.0005)	0.1125 (0.0008)	0.3699 (0.0004)
C <sub>3</sub>	0.7541 (0.0005)	0.0087 (0.0008)	0.2716 (0.0004)
C <sub>4</sub>	0.8880 (0.0005)	-0.1270 (0.0009)	0.3117 (0.0004)
C <sub>5</sub>	0.8638 (0.0005)	-0.3380 (0.0009)	0.3655 (0.0004)
C <sub>6</sub>	0.7893 (0.0004)	-0.3240 (0.0008)	0.4691 (0.0003)
C <sub>7</sub>	0.6291 (0.0004)	-0.2577 (0.0007)	0.4347 (0.0003)

<sup>a</sup> For numbering of atoms, see Fig. 3.**Table 5.** Anisotropic thermal vibration parameters. (Estimated standard deviations in parantheses).

	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
O <sub>1</sub>	0.0134 (0.0003)	0.0347 (0.0011)	0.0073 (0.0002)	0.0010 (0.0009)	0.0051 (0.0004)	0.0004 (0.0007)
O <sub>2</sub>	0.0131 (0.0003)	0.0325 (0.0011)	0.0079 (0.0002)	-0.0057 (0.0009)	0.0067 (0.0004)	-0.0065 (0.0007)
C <sub>1</sub>	0.0130 (0.0004)	0.0308 (0.0016)	0.0070 (0.0003)	-0.0014 (0.0012)	0.0050 (0.0005)	-0.0070 (0.0009)
C <sub>2</sub>	0.0172 (0.0006)	0.0318 (0.0016)	0.0115 (0.0004)	-0.0031 (0.0016)	0.0113 (0.0008)	-0.0001 (0.0013)
C <sub>3</sub>	0.0188 (0.0006)	0.0398 (0.0017)	0.0085 (0.0003)	0.0000 (0.0017)	0.0104 (0.0007)	0.0033 (0.0012)
C <sub>4</sub>	0.0156 (0.0006)	0.0472 (0.0020)	0.0097 (0.0003)	0.0044 (0.0019)	0.0108 (0.0007)	-0.0003 (0.0013)
C <sub>5</sub>	0.0160 (0.0006)	0.0456 (0.0019)	0.0094 (0.0003)	0.0071 (0.0016)	0.0088 (0.0007)	0.0042 (0.0012)
C <sub>6</sub>	0.0168 (0.0006)	0.0345 (0.0016)	0.0081 (0.0003)	0.0065 (0.0015)	0.0062 (0.0006)	0.0037 (0.0011)
C <sub>7</sub>	0.0143 (0.0005)	0.0265 (0.0017)	0.0089 (0.0003)	0.0006 (0.0013)	0.0082 (0.0006)	0.0004 (0.0010)

The actual improvement in the average coordinate E.S.D.'s corresponded to a factor 0.87. The  $R$ -value arrived at for all data was 9.1 %.

A final difference Fourier map, calculated with the observed data and with phases determined by the parameters corresponding to  $R = 7.4$  % contained no larger density fluctuations than  $0.25 \text{ e}\cdot\text{\AA}^{-3}$ , the E.S.D. of the electron density<sup>12</sup> being  $\sigma(\rho) = 0.06 \text{ e}\cdot\text{\AA}^{-3}$ .

The fractional atomic coordinates and the thermal vibration parameters arrived at are given in Tables 4, 5, and 6. The expressions for the anisotropic and isotropic vibrations are:

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

and  $\exp[-B\cdot\sin^2\theta/\lambda^2]$

A comparison between calculated and observed structure factors is presented in Table 7. The accidentally absent reflections (with  $F_o$ -values corresponding to  $I_{\min}$ ) are compared to the calculated values in Table 8.

#### THERMAL MOTIONS

The principal axes of the thermal vibration ellipsoids for the oxygen atoms and the carbon atoms were derived from the temperature parameters in Table 5. Root mean square amplitudes and  $B$ -values for the atomic anisotropic thermal

Table 6. Fractional coordinates and isotropic thermal vibration parameters for hydrogen atoms.<sup>a</sup> (Estimated standard deviations in parantheses).

	$x$	$y$	$z$	$B$ ( $\text{\AA}^2$ )
H <sub>2</sub>	0.642 (0.003)	0.247 (0.005)	0.344 (0.003)	4.3 (0.8)
H <sub>2</sub> '	0.785 (0.003)	0.163 (0.004)	0.425 (0.002)	2.5 (0.6)
H <sub>3</sub>	0.773 (0.003)	0.152 (0.005)	0.214 (0.003)	3.3 (0.7)
H <sub>3</sub> '	0.667 (0.003)	-0.071 (0.004)	0.216 (0.002)	3.0 (0.7)
H <sub>4</sub>	0.963 (0.003)	-0.039 (0.004)	0.371 (0.002)	2.4 (0.6)
H <sub>4</sub> '	0.940 (0.003)	-0.150 (0.005)	0.249 (0.003)	3.7 (0.7)
H <sub>5</sub>	0.969 (0.003)	-0.406 (0.005)	0.403 (0.003)	4.7 (0.8)
H <sub>5</sub> '	0.791 (0.003)	-0.442 (0.005)	0.302 (0.003)	4.4 (0.7)
H <sub>6</sub>	0.785 (0.003)	-0.484 (0.005)	0.504 (0.003)	3.5 (0.7)
H <sub>6</sub> '	0.841 (0.003)	-0.230 (0.005)	0.531 (0.002)	3.7 (0.7)
H <sub>7</sub>	0.577 (0.002)	-0.299 (0.003)	0.345 (0.001)	1.0 (0.5)
H <sub>7</sub> '	0.575 (0.003)	-0.325 (0.006)	0.490 (0.003)	5.2 (0.8)

<sup>a</sup> Referring to Fig. 3 the hydrogen atoms H<sub>n</sub> and H<sub>n</sub>' are bonded to C<sub>n</sub>.

Table 7. Observed and calculated structure factors.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
1	0	0	45.4	-46.7	4	0	10	2.8	2.4	3	1	4	2.6	-3.1	-7	1	11	1.8	-1.5
2	0	0	29.0	-30.3	5	0	10	3.5	-2.9	4	1	4	1.2	1.4	-5	1	11	6.8	6.6
3	0	0	3.8	2.9	6	0	10	1.4	-1.9	5	1	4	10.6	-11.4	-4	1	11	4.5	-3.9
4	0	0	30.5	-26.1	-9	0	12	2.5	-3.7	6	1	4	5.1	-5.1	-3	1	11	9.0	8.9
5	0	0	9.9	9.4	-8	0	12	2.6	-3.0	7	1	4	4.8	4.3	-2	1	11	5.2	-5.3
6	0	0	2.9	-2.5	-7	0	12	1.5	1.5	9	1	4	4.2	3.8	-1	1	11	4.1	-4.2
7	0	0	6.2	-6.4	-6	0	12	1.7	-2.1	-11	1	5	1.5	1.3	0	1	11	5.1	5.5
8	0	0	9.7	2.1	-5	0	12	3.2	2.8	-9	1	5	2.1	-1.6	1	1	11	5.6	-6.5
9	0	0	2.4	2.8	-2	0	12	5.3	6.0	-8	1	5	10.1	-9.6	2	1	11	1.4	1.0
10	0	0	1.2	-1.3	0	0	12	7.3	-8.1	-7	1	5	3.5	3.1	4	1	11	4.5	4.0
11	0	0	2.1	1.4	1	0	12	4.3	4.4	-6	1	5	9.3	9.7	5	1	11	1.8	-1.4
-11	0	0	4.3	4.8	2	0	12	2.9	-3.1	-5	1	5	11.8	-10.5	-8	1	12	2.4	2.3
-10	0	0	4.1	3.9	3	0	12	2.6	2.7	-4	1	5	23.7	24.0	-6	0	12	2.6	2.0
-9	0	0	7.2	-6.7	4	0	12	1.3	-1.4	-3	1	5	5.3	-4.5	-5	1	12	1.3	1.1
-8	0	0	10.4	10.3	-6	0	14	.7	1.4	-2	1	5	3.4	3.2	-3	1	12	3.0	2.5
-7	0	0	24.7	-24.7	-5	0	14	4.0	4.5	-1	1	5	23.1	-23.7	-2	1	12	2.3	2.3
-6	0	0	10.4	10.8	-4	0	14	4.0	-4.6	0	1	5	15.7	15.1	-1	1	12	3.8	-3.4
-5	0	0	10.6	10.8	-3	0	14	1.0	1.0	-1	1	5	15.9	-23.5	0	1	12	1.8	-1.9
-4	0	0	7.8	-8.7	-2	0	14	2.2	-2.7	2	1	5	11.3	11.3	2	1	12	3.3	3.4
-3	0	0	19.1	18.2	1	0	14	1.0	-1.5	3	1	5	2.6	2.7	3	1	12	1.5	1.2
-2	0	0	27.4	26.4	1	1	0	32.2	-36.4	4	1	5	7.4	-7.2	4	1	12	2.6	-3.0
-1	0	0	17.7	16.0	2	1	0	27.5	-28.5	5	1	5	10.3	11.1	-6	1	13	2.1	2.0
0	0	0	32.4	32.4	3	1	0	25.4	-27.1	6	1	5	3.2	-2.7	-5	1	13	1.1	-1.0
1	0	0	97.3	-97.1	4	1	0	17.3	16.0	7	1	5	2.1	-1.8	-4	1	13	2.2	-2.3
2	0	0	21.8	-18.9	5	1	0	3.9	3.7	-11	1	6	1.9	-1.9	-3	1	13	2.9	-2.5
3	0	0	15.6	16.6	7	1	0	4.7	4.5	-9	1	6	2.0	-2.1	-2	1	13	3.3	3.1
4	0	0	29.5	-29.6	8	1	0	1.5	1.8	-8	1	6	2.1	-1.4	-1	1	13	2.0	-1.5
5	0	0	33.0	32.7	9	1	0	2.1	-2.4	-7	1	6	6.4	6.4	0	1	13	2.0	-1.5
6	0	0	3.1	2.9	11	1	0	1.9	-1.5	-6	1	6	4.7	-4.9	1	1	13	1.5	-1.5
8	0	0	5.7	-5.5	-11	1	1	2.9	-2.8	-5	1	6	2.5	-2.4	2	1	13	2.8	3.1
10	0	0	2.0	-1.8	-9	1	1	4.0	3.8	-4	1	6	3.1	-2.3	-6	1	14	.5	.7
11	0	0	1.4	-1.7	-8	1	1	5.7	-5.8	-3	1	6	11.9	-10.8	-5	1	14	1.7	-2.0
-11	0	0	2.3	1.8	-7	1	1	12.3	11.7	-2	1	6	20.3	20.9	-6	1	14	1.7	-2.0
-9	0	0	5.4	-5.0	-6	1	1	2.4	-2.2	-1	1	6	15.7	-15.5	-3	1	14	1.8	2.3
-8	0	0	9.7	10.0	-5	1	1	2.4	-2.4	0	1	6	20.2	-21.3	0	1	14	1.1	1.3
-7	0	0	13.9	-14.3	-4	1	1	2.1	-2.0	1	1	6	7.6	7.4	1	1	14	1.9	.3
-6	0	0	5.8	6.6	-3	1	1	3.6	-3.4	2	1	6	5.3	-4.9	1	2	0	34.1	34.0
-5	0	0	25.4	23.9	-2	1	1	22.5	-23.0	3	1	6	3.6	-3.8	1	2	0	28.7	-31.0
-4	0	0	5.9	-5.9	-1	1	1	24.3	25.7	4	1	6	3.4	-3.7	2	2	0	7.8	6.8
-2	0	0	46.1	-47.5	0	1	1	58.7	-59.7	5	1	6	3.5	-3.4	3	2	0	5.6	5.6
-1	0	0	8.1	7.7	1	1	1	72.6	75.0	6	1	6	1.5	2.1	4	2	0	10.7	10.5
0	0	0	18.3	-18.0	2	1	1	7.5	-8.0	7	1	6	4.6	3.9	5	2	0	4.6	-4.7
1	0	0	21.6	21.8	3	1	1	33.2	-36.9	-11	1	7	2.2	-2.2	6	2	0	1.7	-1.8
2	0	0	14.0	-13.4	4	1	1	27.9	29.0	-8	1	7	9.3	9.3	-10	2	1	1.2	1.1
3	0	0	9.4	9.3	5	1	1	1.6	2.2	-7	1	7	6.3	-5.8	-9	2	1	2.0	1.2
4	0	0	11.9	12.4	6	1	1	2.8	2.2	-6	1	7	6.9	6.9	-8	2	1	2.1	2.1
5	0	0	8.0	8.2	7	1	1	6.2	-6.1	-5	1	7	4.4	3.3	-7	2	1	3.4	-3.6
6	0	0	12.1	-12.9	-8	1	1	2.0	-1.5	-4	1	7	3.8	-3.8	-6	2	1	4.0	3.9
7	0	0	7.3	-6.8	-9	1	1	2.1	2.0	-3	1	7	12.5	-12.5	-5	2	1	10.0	-9.2
9	0	0	3.0	2.2	10	1	1	2.0	-1.4	-2	1	7	13.0	-12.7	-4	2	1	6.7	-8.0
10	0	0	1.8	1.4	-9	1	2	1.5	-1.3	-1	1	7	8.5	8.3	-3	2	1	3.3	-3.3
-10	0	0	1.8	1.7	-8	1	2	8.2	-8.5	0	1	7	13.5	13.2	-2	2	1	4.4	3.4
-9	0	0	5.1	4.3	-7	1	2	6.7	6.1	1	1	7	7.9	-7.3	-1	2	1	43.6	43.1
-8	0	0	11.3	-11.2	-6	1	2	9.4	9.3	2	1	7	1.9	-1.8	0	2	1	11.7	-13.3
-7	0	0	2.0	1.8	-5	1	2	5.2	-4.5	3	1	7	12.3	11.4	1	2	1	22.0	-24.3
-6	0	0	4.5	3.5	-4	1	2	13.1	13.6	4	1	7	12.6	-12.2	2	2	1	15.1	17.7
-5	0	0	12.6	11.6	-3	1	2	3.6	-3.7	5	1	7	6.7	6.2	3	2	1	11.6	13.0
-4	0	0	24.0	-23.1	-2	1	2	12.6	-11.6	6	1	7	6.4	-7.8	4	2	1	11.4	-13.4
-3	0	0	15.1	-12.1	-1	1	2	1.7	1.3	7	1	7	3.4	3.1	5	2	1	6.9	8.4
-1	0	0	25.2	24.2	0	1	2	31.8	-34.1	-11	1	8	1.8	-1.7	6	2	1	7.9	-8.6
0	0	0	13.9	-12.9	1	1	2	23.9	-25.6	-10	1	8	1.1	1.0	7	2	1	4.0	-3.9
1	0	0	15.2	14.2	2	1	2	5.6	5.9	-7	1	8	5.8	5.1	8	2	1	3.6	3.4
2	0	0	3.0	-2.7	3	1	2	13.1	15.0	-6	1	8	5.8	-5.1	-10	2	2	1.6	1.9
3	0	0	11.9	-12.7	4	1	2	28.3	29.1	-5	1	8	3.2	-3.2	-9	2	2	6.8	6.8
4	0	0	16.4	16.3	5	1	2	8.0	-8.4	-3	1	8	3.5	3.5	-8	2	2	6.5	6.8
5	0	0	17.5	-17.9	6	1	2	8.8	-5.8	-2	1	8	8.2	6.1	-7	2	2	3.9	-4.0
6	0	0	1.3	1.2	7	1	2	2.1	1.6	0	1	8	8.0	-7.6	-6	2	2	7.5	7.1
7	0	0	3.6	3.7	8	1	2	5.4	-5.4	1	1	8	2.7	2.5	-5	2	2	1.6	2.0
9	0	0	7.3	-6.8	9	1	2	1.4	1.4	2	1	8	1.4	-1.0	-4	2	2	5.9	-5.4
-10	0	0	1.6	-1.9	-11	1	3	1.5	-1.4	3	1	8	2.9	3.0	-3	2	2	8.6	-8.2
-8	0	0	10.1	-10.0	-10	1	3	1.3	.7	4	1	8	2.5	2.5	-2	2	2	32.4	32.9
-7	0	0	15.6	16.6	-9	1	3	12.7	12.4	5	1	8	3.2	-2.9	-1	2	2	24.8	-25.6
-6	0	0	3.5	-2.8	-8	1	3	14.2	-14.3	7	1	8	1.2	-1.2	0	2	2	9.0	-8.2
-5	0	0	9.5	-9.7	-7	1	3	5.8	5.7	-10	1	9	2.4	2.3	1	2	2	5.1	4.8
-4	0	0	17.8	17.4	-6	1	3	8.9	-8.6	-9	1	9	1.2	-1.8	2	2	2	4.1	4.1
-3	0	0	15.1	-14.2	-5	1	3	5.3	-5.5	-7	1	9	6.7	-6.3	3	2	2	18.9	22.3
-2	0	0	7.8	7.3	-4	1	3	13.4	13.9	-6	1	9	1.5	2.1	4	2	2	17.3	-18.7
-1	0	0	3.3	3.2	-3	1	3	10.9	-10.8	-5	1	9	4.1	2.9	5	2	2	2.1	-2.4
0	0	0	2.8	-2.5	-2	1	3	1.8	1.6	-4	1	9	21.6	-22.1	6	2	2	1.3	-1.5
1	0	0	3.2	2.6	-1	1	3	26.0	29.1	-3	1	9	19.5	18.1	7	2	2	5.0	5.5
2	0	0	3.8	-3.2	0	1	3	19.3	20.0	-2	1	9	2.0	1.1	8	2	2	5.0	-5.6
3	0	0	10.5	-10.2	1	1	3	23.9	-23.6	-1	1	9	5.2	4.4	9	2	2	3.2	2.9
4	0	0	16.9	16.3	2	1	3	1.4	.7	1	1	9	3.2	-3.7	-11	2	3	2.1	2.1



Table 7. Continued.

k	h	l	F <sub>0</sub>	F <sub>z</sub>	k	h	l	F <sub>0</sub>	F <sub>z</sub>	k	h	l	F <sub>0</sub>	F <sub>z</sub>	k	h	l	F <sub>0</sub>	F <sub>z</sub>
-10	2	4	1.8	1.3	-2	2	11	1.4	-3	0	3	6	13.1	-13.9	4	4	3	7.5	-7.9
-9	2	4	6.1	-5.9	-1	2	11	4.7	-4.2	1	3	6	4.2	3.6	5	4	3	6.7	6.6
-8	2	4	13.4	13.0	0	2	11	4.6	-3.8	3	3	6	3.0	-4.0	6	4	3	2.6	2.7
-7	2	4	2.0	-1.7	1	2	11	7.8	7.0	4	3	6	1.1	-7.7	7	4	3	3.5	-3.6
-6	2	4	10.8	-9.8	2	2	11	1.3	1.5	5	3	6	6.2	4.9	8	4	3	3.1	3.1
-5	2	4	4.2	4.1	3	2	11	2.1	-2.3	6	3	7	2.9	2.8	9	4	3	2.3	-2.5
-4	2	4	9.3	-8.8	-7	2	12	.9	1.6	-7	3	7	8.2	-8.0	-6	4	4	2.6	2.4
-3	2	4	14.2	14.2	-5	2	12	4.5	-5.0	-5	2	12	4.5	-5.0	-4	4	4	2.6	2.4
-2	2	4	10.3	-9.7	-4	2	12	3.1	3.0	-4	2	12	3.1	3.0	-3	4	4	10.3	-10.3
-1	2	4	6.2	-5.4	-3	2	12	1.8	1.1	-3	3	7	10.3	10.1	-2	4	4	3.2	2.5
0	2	4	5.3	-4.9	-2	2	12	2.9	-3.0	-2	2	12	2.9	-3.0	-2	4	4	16.7	14.7
1	2	4	24.6	26.5	-1	2	12	1.8	1.8	-1	2	12	1.8	1.8	-1	4	4	18.9	-16.4
2	2	4	20.5	-21.7	0	2	12	2.5	-2.3	-1	3	7	7.6	-7.2	-1	4	4	12.1	-11.0
3	2	4	3.3	2.9	1	2	12	3.9	4.2	0	3	7	3.4	3.1	0	4	4	2.7	2.1
4	2	4	3.7	-3.1	4	2	12	1.7	-2.1	1	3	7	3.5	-3.7	2	4	4	4.8	-4.4
5	2	4	2.3	-2.0	-7	2	13	1.5	2.1	2	3	7	8.3	-7.8	3	4	4	7.2	-7.3
6	2	4	3.2	2.8	-6	2	13	2.1	-2.6	3	3	7	7.0	7.2	4	4	4	2.6	2.7
7	2	4	2.3	1.8	-5	2	13	2.4	-2.4	4	3	7	4.9	-4.9	5	4	4	2.6	2.6
8	2	4	3.5	-3.1	1	2	13	1.8	1.9	5	3	7	6.0	5.6	6	4	4	4.7	4.4
-10	2	5	1.5	-1.7	-5	2	14	1.3	1.8	-9	3	8	5.0	5.2	-7	4	5	3.6	-4.6
-7	2	5	6.8	6.7	-2	2	14	2.2	-2.6	-8	3	8	5.8	-5.1	-6	4	5	2.6	-1.7
-6	2	5	12.8	11.7	-1	2	14	1.8	2.4	-7	3	8	5.1	3.1	-5	4	5	6.4	6.1
-5	2	5	3.1	2.8	1	3	2	17.1	17.2	-6	3	8	6.2	4.8	-4	4	5	10.3	9.1
-4	2	5	22.8	-21.7	2	3	0	21.0	-22.0	-2	3	8	6.7	-6.4	-2	4	5	4.3	-3.6
-3	2	5	1.5	-1.7	3	3	0	5.8	-5.6	-1	3	8	6.3	5.2	-1	4	5	8.8	-8.8
-2	2	5	8.9	-8.0	4	3	0	10.6	9.5	0	3	8	4.2	-4.5	0	4	5	10.8	-10.2
-1	2	5	17.5	-18.2	5	3	0	9.6	-9.1	1	3	8	2.2	1.6	1	4	5	2.6	2.7
0	2	5	15.8	17.5	6	3	1	5.3	-5.1	2	3	8	5.5	5.5	2	4	5	3.5	2.7
1	2	5	9.2	9.0	-7	3	1	7.1	7.3	3	3	8	5.3	-4.6	3	4	5	3.5	2.7
2	2	5	10.2	10.1	-6	3	1	5.3	-4.1	4	3	8	3.0	3.1	4	4	5	3.1	-3.3
3	2	5	1.9	-2.0	-5	3	1	9.0	-8.0	-9	3	9	4.0	-3.5	-4	4	6	3.5	3.8
4	2	5	6.2	-6.5	-4	3	1	7.7	7.1	-8	3	9	2.1	1.7	-7	4	6	2.6	-2.3
5	2	5	11.6	-11.0	-3	3	1	14.1	13.4	-6	3	9	5.7	4.9	-5	4	6	14.2	-12.1
6	2	5	1.0	-1.2	-2	3	1	7.5	-7.4	-5	3	9	4.9	-4.2	0	4	6	11.2	-11.1
-10	2	6	1.1	1.0	-1	3	1	8.1	9.0	-4	3	9	4.9	-4.2	1	4	6	4.8	-3.6
-9	2	6	7.9	-7.8	0	3	1	32.6	-32.3	-3	3	9	7.7	8.4	2	4	6	9.6	8.3
-8	2	6	10.5	10.5	1	3	1	16.8	19.0	-2	3	9	8.0	-9.4	3	4	6	2.6	-2.6
-7	2	6	12.7	-12.6	2	3	1	1.4	-1.4	-1	3	9	4.4	2.6	4	4	6	3.7	4.5
-6	2	6	6.5	6.0	3	3	1	1.7	1.6	1	3	9	5.7	5.1	-9	4	7	1.8	-1.7
-5	2	6	5.3	5.7	4	3	1	9.3	-9.2	2	3	9	2.1	2.0	-8	4	7	2.2	1.9
-4	2	6	4.9	5.2	5	3	1	5.5	6.0	3	3	9	4.8	-4.5	-7	4	7	3.4	-4.1
-3	2	6	11.6	-11.0	6	3	1	2.0	-2.7	-9	3	10	2.8	3.3	-5	4	7	4.5	4.1
-2	2	6	5.3	5.0	-9	3	2	2.0	-2.5	-8	3	10	4.3	-4.2	0	4	7	10.0	-9.7
-1	2	6	1.7	-1.4	-7	3	2	4.3	4.2	-5	3	10	6.3	-6.1	1	4	7	3.6	-2.4
0	2	6	1.9	-2.0	-6	3	2	4.9	-4.8	-4	3	10	3.7	4.2	2	4	7	1.5	3.0
1	2	6	5.8	6.4	-5	3	2	5.7	6.2	-3	3	10	3.7	-3.8	-6	4	7	1.7	2.6
2	2	6	9.4	-9.2	-4	3	2	5.2	4.9	-1	3	10	3.1	3.1	-5	4	7	4.4	-3.8
3	2	6	7.8	8.1	-3	3	2	10.6	-9.8	0	3	10	4.3	3.3	-4	4	8	5.8	5.7
-11	2	7	1.8	2.5	-2	3	2	8.3	7.7	1	3	10	5.2	-3.8	-3	4	8	3.7	-4.0
-10	2	7	1.0	1.8	-1	3	2	26.6	-27.9	2	3	10	2.3	2.7	0	4	8	2.6	2.6
-9	2	7	1.8	-1.2	0	3	2	5.9	6.0	3	3	10	3.3	-3.0	1	4	8	4.6	5.9
-8	2	7	6.5	6.5	1	3	2	1.9	2.0	-8	3	11	3.3	3.9	2	4	8	2.6	2.6
-7	2	7	5.2	-5.8	2	3	2	7.4	-7.2	-6	3	11	4.3	-4.1	3	4	8	6.8	-6.5
-6	2	7	9.7	-9.6	3	3	2	5.6	6.4	-5	3	11	2.7	2.1	4	4	8	3.3	3.4
-5	2	7	8.9	-8.5	4	3	2	9.4	10.3	-4	3	11	2.9	-2.0	5	4	8	1.7	2.1
-4	2	7	4.0	3.9	-5	3	2	12.7	-12.0	-3	3	11	2.0	2.0	-7	4	9	2.1	-2.6
-3	2	7	10.9	11.3	6	3	2	5.2	4.7	-2	3	11	4.6	-5.4	-3	4	9	5.1	-4.6
-2	2	7	1.7	1.0	7	3	2	2.2	1.0	-1	3	11	2.0	1.4	0	4	9	3.6	2.4
0	2	7	10.9	12.2	-8	3	2	3.0	-4.8	0	3	11	6.7	6.1	1	4	9	4.2	-3.0
1	2	7	8.8	-8.9	-10	3	3	4.2	-4.0	2	3	11	4.5	-4.6	2	4	10	2.5	-2.9
2	2	7	1.9	-1.9	-8	3	3	3.1	-3.4	-6	3	12	2.0	1.6	-4	4	10	3.3	3.7
3	2	7	5.0	2.5	-7	3	3	9.9	8.9	-4	3	12	2.4	2.8	-3	4	10	4.8	-4.8
4	2	7	5.6	-6.0	-6	3	3	5.0	-5.3	1	3	12	2.3	-2.3	-2	4	10	4.2	4.3
5	2	7	2.1	-2.2	-5	3	3	6.3	6.0	0	4	0	7.9	7.3	-1	4	10	2.4	-1.6
6	2	7	3.1	3.2	-4	3	3	6.8	6.7	1	4	2	16.5	-17.5	2	4	10	4.3	-3.3
-10	2	8	2.5	-3.0	-3	3	3	17.6	-16.3	2	4	0	5.6	5.7	-1	4	11	3.1	3.2
-9	2	8	3.5	3.7	-2	3	3	1.3	-1.3	3	4	0	3.1	2.3	1	4	11	2.8	3.0
-8	2	8	4.6	-4.9	-1	3	3	2.4	-1.8	5	4	0	8.7	9.0	2	4	11	2.5	-3.3
-7	2	8	4.1	-3.8	0	3	3	1.7	-1.9	6	4	0	3.6	-2.8	-1	4	12	1.7	2.6
-6	2	8	10.4	10.5	2	3	3	13.9	14.8	7	4	0	3.8	-3.2	1	4	12	2.0	2.2
-5	2	8	1.9	1.9	3	3	3	7.8	-7.6	8	4	0	2.4	2.0	1	5	0	2.5	1.6
-4	2	8	5.2	5.2	4	3	3	4.0	4.5	-6	4	1	2.5	2.7	2	5	0	6.9	8.6
-3	2	8	3.3	2.5	-5	3	3	2.2	-1.0	-5	4	1	3.3	-3.5	3	5	0	3.5	-3.2
-2	2	8	3.6	3.9	6	3	3	2.9	3.1	-4	4	1	3.0	3.0	-3	5	1	4.9	4.4
-1	2	8	2.4	2.5	-10	3	4	1.7	1.9	-3	4	1	1.8	1.1	-2	5	1	4.9	-4.8
0	2	8	6.5	-6.3	-8	3	4	3.1	3.0	-2	4	1	8.4	-9.3	-1	5	1	3.0	2.8
1	2	8	2.8	2.8	-6	3	4	2.9	-3.2	0	4	1	3.2	2.6	0	5	1	4.1	4.5
2	2	8	2.8	2.2	-5	3	4	5.4	-5.2	1	4	1	4.7	5.2	1	5	1	6.1	-6.0
-9	2	9	4.8	-4.7	-4	3	4	8.6	8.8	2	4	1	3.8	4.2	2	5	1	6.1	4.7
-8	2	9	3.4	2.6	-3	3	4	16.7	-14.6	3	4	1	15.3	-15.9	-5	5	2	3.0	-3.6
-7	2	9	5.2	-5.0	-2	3	4	3.3	2.2	4	4	1	8.3	8.2	-4	5	2	4.8	4.1
-6	2	9	3.8	-3.3	-1	3	4	6.9	6.3	-7	4	2	3.7	-5.1	-3	5	2	6.8	-7.2
-5	2	9	5.0	5.1	0	3	4	6.5	6.3	-6	4	2	11.1	12.2	-2	5	2	4.3	3.6
-4	2	9	5.8	4.5	1	3	4	4.8	-4.9	-5	4	2	3.4	-2.8	-1	5	2	3.7	3.5
-3	2	9	3.0	3.7	-9														

Table 7. *Continued.*

<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$
0	5	5	2.8	2.5
1	5	5	4.1	3.5
-4	5	5	6.4	7.2
-3	5	5	4.3	-4.5
-2	5	5	4.2	-3.5
-1	5	5	4.2	4.1
0	5	5	6.0	-5.8
1	5	5	7.7	8.3
2	5	5	4.4	-4.0
0	5	7	4.4	3.8
4	5	7	5.3	-5.5
3	5	7	4.2	2.0

Table 8. Unobserved and calculated structure factors (The  $F_u$ 's have been obtained by taking unobserved intensities as equal to the smallest observable).

<i>h</i>	<i>k</i>	<i>l</i>	$F_u$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_u$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_u$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_u$	$F_c$
7	0	2	1.3	1.5	3	1	13	.7	-0.0	-4	2	13	1.1	.0	7	3	5	1.4	-1.1
-10	0	4	1.2	-1.0	-2	1	14	1.0	-1.4	-3	2	13	1.1	.7	-7	3	9	2.1	.6
-3	0	4	.9	.8	-1	1	14	.9	-1.1	-2	2	13	1.1	1.1	0	3	9	2.5	-1.3
8	0	4	1.3	-0.8	5	2	0	1.1	-0.6	-1	2	13	1.1	.8	5	3	9	1.9	1.3
-11	0	6	.9	.4	7	2	0	1.4	.3	0	2	13	1.0	.0	0	3	9	1.5	.5
-2	0	6	1.0	.9	8	2	0	1.5	.4	2	2	13	.8	-0.5	-7	3	10	1.9	1.7
8	0	6	1.2	.5	9	2	0	1.4	-.2	-4	2	14	.8	.3	-6	3	10	2.1	.4
-9	0	6	1.2	-.7	11	2	0	.9	1.0	-3	2	14	.8	.6	-3	3	10	2.5	1.1
1	0	10	1.4	1.2	-11	2	1	.9	1.1	0	2	14	.6	.2	4	3	10	1.8	.3
-5	0	12	1.2	-.9	9	2	1	1.4	-.3	7	3	0	2.3	-1.5	5	3	10	1.5	-.2
-3	0	12	1.3	.3	10	2	1	1.2	.2	8	3	0	2.3	-.0	6	3	10	.5	-.7
-1	0	12	1.5	-.3	11	2	1	.8	.6	7	3	0	2.1	1.3	-7	3	11	1.6	-1.1
-1	0	14	.8	-1.1	-11	2	2	1.0	-.1	10	3	0	1.7	-1.8	1	3	11	2.0	.4
0	0	14	.8	.6	10	2	2	1.1	-.7	-10	3	1	1.8	.2	2	3	11	1.9	1.4
6	1	0	1.3	-.4	-9	2	3	1.4	-.9	-9	3	1	2.2	-1.4	4	3	11	1.4	-.7
-10	1	1	1.4	-.6	2	2	3	1.9	-.2	2	3	1	1.2	-.6	-5	3	12	1.7	-.5
8	1	1	1.4	.6	10	2	3	1.0	-.3	6	3	1	1.5	.0	-3	3	12	1.9	-1.7
-11	1	2	1.1	.6	-11	2	4	1.0	-.7	4	3	1	2.1	.3	-2	3	12	1.9	-.2
-10	1	2	1.4	.1	7	2	4	1.5	.4	10	3	1	1.0	1.1	-1	3	12	1.9	.2
11	1	2	.8	-.6	8	2	4	1.4	-.9	-10	3	2	1.0	1.5	0	3	12	1.8	.3
6	1	3	1.5	-.5	10	2	4	.8	-.9	-8	3	2	2.3	-.1	2	3	12	1.5	-.9
7	1	3	1.5	-.5	-11	2	5	.9	-.7	9	3	2	2.0	2.2	-3	3	12	1.1	-.4
10	1	3	1.1	.8	-8	2	5	1.5	-.2	10	3	2	1.4	-1.0	4	4	0	1.2	.5
-11	1	3	.5	1.3	6	2	5	1.5	-.3	-9	3	3	2.2	1.9	-1	4	1	.6	-.4
-11	1	4	1.1	-.8	7	2	5	1.4	-.5	1	3	3	1.4	-1.7	3	4	2	.8	2.0
-10	1	4	1.4	1.0	10	2	5	.4	-.3	3	3	3	1.8	.6	3	4	2	1.2	.7
8	1	4	1.5	-.9	-11	2	6	.8	.7	4	3	3	2.0	1.3	5	4	2	1.4	2.3
10	1	4	1.0	-.2	-9	2	6	1.4	.3	4	3	3	1.6	-1.6	-1	4	3	.9	-.6
-10	1	5	1.4	-.2	-8	2	6	1.5	.2	10	3	3	1.2	-1.4	1	4	4	1.1	.7
8	1	5	1.4	-.4	-7	2	6	1.5	-1.1	-7	3	4	2.3	-.4	4	4	4	1.4	-.1
9	1	5	1.2	-.2	7	2	6	1.4	-.6	6	3	4	1.5	-1.4	2	4	5	1.3	-.8
10	1	5	1.4	-.6	8	2	6	1.2	-1.1	2	3	4	1.6	1.4	3	4	5	1.4	.3
-10	1	6	1.3	.6	9	2	6	.8	-.3	3	3	4	1.9	-1.1	4	4	5	1.5	-.6
8	1	6	1.3	.2	-7	2	7	1.5	1.1	0	3	4	2.3	-.2	-3	4	5	1.4	-.3
9	1	6	1.0	-.1	7	2	7	1.2	1.5	5	3	4	2.3	-.5	-6	4	7	1.5	1.0
-10	1	7	1.2	-.5	8	2	7	1.0	-.1	7	3	4	2.3	1.6	-4	4	7	1.5	-.9
-9	1	7	1.4	-.2	-9	2	8	1.2	.8	8	3	4	2.0	-1.9	-3	4	7	1.4	-.7
7	1	7	1.4	-.2	-6	2	8	1.4	-.6	-10	3	5	1.7	-.0	-2	4	7	1.4	-1.0
9	1	7	.7	-.9	-3	2	8	1.4	.4	-6	3	5	2.3	-.9	-2	4	8	1.5	1.2
-9	1	8	1.4	.3	7	2	8	1.1	-1.1	-3	3	5	1.0	-.5	-1	4	8	1.5	-.5
-10	1	8	1.4	-.2	8	2	8	.7	-1.2	-2	3	5	1.3	1.8	-2	4	8	1.5	-.6
-10	1	8	1.5	-1.0	-10	2	9	.6	-.3	7	3	5	2.4	-.5	-1	4	9	1.5	1.4
-5	1	8	1.5	-1.7	2	2	9	1.5	-.7	8	3	5	1.9	.3	1	4	9	1.4	2.6
0	1	8	1.4	1.0	4	2	9	1.4	-.4	9	3	5	1.3	-.8	0	4	10	1.4	-1.0
8	1	8	.9	.1	5	2	9	1.3	1.4	-10	3	6	1.6	-1.2	1	4	10	1.3	2.0
-6	1	9	1.4	1.6	6	2	9	1.1	1.0	-9	3	6	1.2	1.2	0	4	11	1.2	-2.1
0	1	9	1.5	.1	7	2	9	.8	-.1	-3	3	6	2.0	.8	0	4	12	.9	1.4
2	1	9	1.0	-1.4	-10	2	10	.4	-.6	2	3	6	2.1	.4	1	5	1	.9	.8
3	1	9	1.0	1.1	-8	2	10	1.2	-1.0	0	3	6	2.2	-1.7	3	5	1	1.3	-1.1
0	1	9	1.2	.6	0	2	10	1.5	-.6	7	3	6	2.0	1.3	0	5	2	1.0	.2
-6	1	10	1.3	-.4	1	2	10	1.5	-.6	8	3	6	1.8	.4	-4	5	3	1.5	1.9
-7	1	10	1.4	.5	2	2	10	1.4	1.0	-10	3	7	1.5	2.0	-2	5	3	1.2	1.4
-6	1	10	1.6	-.1	3	2	10	1.1	-.4	-9	3	7	1.9	-.6	-1	5	3	1.2	1.5
0	1	10	1.0	.6	0	2	10	.6	-.9	-5	3	7	2.3	-.8	0	5	3	1.2	1.4
7	1	10	.4	-.1	-9	2	11	.7	-1.1	6	3	7	2.1	-.9	2	5	3	1.4	-2.1
-5	1	11	1.1	-.7	-3	2	11	1.4	-.6	7	3	7	1.8	.6	3	5	3	1.5	2.9
-6	1	11	1.0	-.9	3	2	11	1.2	.9	0	3	7	1.2	.0	2	5	3	1.0	-1.2
3	1	11	.3	.7	4	2	11	1.0	.1	-10	3	8	1.2	-1.2	3	5	3	1.0	.2
-7	1	12	1.1	-.5	-8	2	12	.7	-.4	-4	3	8	2.3	-.5	3	5	6	1.6	.8
-6	1	12	1.4	-.3	-6	2	12	1.1	-.6	-3	3	8	2.3	2.8	-1	5	7	1.6	-.2
0	1	12	1.4	1.0	2	2	12	1.1	-1.3	5	3	8	2.1	-.6	1	5	7	1.6	-.9
-7	1	13	.6	.1	3	2	12	.9	-1.1	6	3	8	1.8	-2.1					

vibrations along the principal axes as well as the components of these axes along the crystal axes are given in Table 9.

The atomic vibration tensors referred to crystal axes were calculated according to Scheringer<sup>13</sup> and applied in a rigid-body analysis of translational and librational motion of the molecule about the centre of symmetry.<sup>14,\*</sup>

\* The programme has been modified by cand.real. F. Gram at this university.

The  $T$  and  $\omega$  tensors were calculated in an orthogonal coordinate system defined by the principal inertial axes of the molecule. The results are given in Tables 10 and 11.

Table 9. 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>	0.011	0.155	0.004	0.269	5.70
	0.108	-0.016	0.029	0.239	4.53
	0.013	0.001	-0.083	0.216	3.69
O <sub>2</sub>	0.047	-0.127	0.042	0.277	6.07
	0.095	0.077	0.020	0.227	4.06
	0.025	-0.050	-0.074	0.210	3.47
C <sub>1</sub>	0.017	-0.138	0.041	0.266	5.58
	0.107	0.023	0.013	0.235	4.35
	0.001	-0.071	-0.076	0.197	3.06
C <sub>2</sub>	0.088	0.013	0.065	0.259	5.31
	0.004	-0.156	0.003	0.234	4.34
	0.064	-0.002	-0.058	0.220	3.81
C <sub>3</sub>	0.075	0.111	0.025	0.286	6.45
	0.079	-0.102	-0.006	0.250	4.93
	0.007	-0.041	0.084	0.226	4.02
C <sub>4</sub>	0.039	0.143	0.024	0.316	7.89
	0.085	-0.064	0.055	0.261	5.37
	0.055	-0.002	-0.064	0.230	4.18
C <sub>5</sub>	0.023	0.152	0.006	0.315	7.83
	0.084	-0.028	0.066	0.276	6.05
	0.065	-0.016	-0.057	0.214	3.63
C <sub>6</sub>	0.070	0.109	0.039	0.292	6.74
	0.077	-0.109	0.022	0.286	6.44
	0.032	0.025	-0.075	0.214	3.62
C <sub>7</sub>	0.082	-0.022	0.069	0.294	6.84
	0.014	-0.145	-0.028	0.258	5.27
	0.070	0.054	-0.046	0.236	4.39

Table 10. Components of atomic vibration tensors  $U_c$  ( $\times 10^4$  Å<sup>2</sup>) referred to crystal axes; as calculated from the thermal parameters obtained by least squares refinement (EXP.), their estimated standard deviations (E.S.D.), and as calculated from rigid-body parameters (R.B.)

		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O <sub>1</sub>	EXP.	600	720	502	15	142	7
	E.S.D.	15	23	14	14	11	13
	R.B.	622	691	497	0	146	-18

Table 10. Continued.

		$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
$O_2$	EXP.	584	673	543	-86	186	-121
	E.S.D.	15	23	15	14	11	13
	R.B.	585	687	557	-83	145	-96
$C_1$	EXP.	580	638	484	-21	137	-131
	E.S.D.	19	32	18	18	14	17
	R.B.	592	604	513	-52	156	-27
$C_2$	EXP.	637	550	614	9	228	7
	E.S.D.	21	35	20	20	16	20
	R.B.	677	614	572	-13	200	-31
$C_3$	EXP.	749	714	561	98	173	69
	E.S.D.	25	32	21	28	18	20
	R.B.	744	805	597	129	226	38
$C_4$	EXP.	715	945	651	108	243	78
	E.S.D.	25	39	23	25	19	23
	R.B.	749	873	619	133	241	11
$C_5$	EXP.	698	978	669	66	300	-5
	E.S.D.	25	42	23	26	20	25
	R.B.	700	922	683	34	283	6
$C_6$	EXP.	839	824	587	0	288	61
	E.S.D.	28	35	22	25	21	22
	R.B.	776	822	670	47	326	71
$C_7$	EXP.	770	658	795	-47	313	-1
	E.S.D.	27	34	28	24	22	24
	R.B.	720	680	698	-54	303	12

Table 11. Principal moments of inertia of the molecule (a.m.u. Å<sup>2</sup>), unit vectors along principal axes, L, M, N, defining the molecular coordinate system, and the rigid-body tensors referred to this coordinate system.

Axis	Moment	$x$	$y$	$z$	
L	416.7	0.0807	-0.0427	-0.0386	
M	2296.2	0.0160	-0.1290	0.0494	
N	2484.8	0.0714	0.0773	0.0612	
	$T = \begin{pmatrix} 545 & 68 & 32 \\ & 585 & 11 \\ & & 508 \end{pmatrix} \times 10^{-4} \text{ Å}^2$				
	$\omega = \begin{pmatrix} 89 & 3 & -11 \\ & 14 & 5 \\ & & 10 \end{pmatrix} \times 10^{-4} \text{ rad}^2$				
			Direction cosines		
	Eigenvalues	r.m.s. values	L	M	N
T	{0.0641 Å <sup>2</sup>	0.253 Å	0.6067	0.7666	0.2101
	{0.0517 »	0.227 »	-0.4015	0.5237	-0.7512
	{0.0479 »	0.218 »	-0.6860	0.3714	0.6256
$\omega$	{0.0090 rad <sup>2</sup>	5.45°	-0.9911	-0.0264	0.1300
	{0.0017 »	2.42°	0.0474	0.8447	0.5330
	{0.0005 »	1.35°	-0.1239	0.5345	-0.8360

Table 12. Corrections in fractional atomic coordinates due to rigid-body motion compared with the estimated standard deviations of the coordinates. (The  $\sigma$ 's and  $\Delta$ 's have been multiplied by  $10^4$ ).

	$\Delta x$	$\sigma x$	$\Delta y$	$\sigma y$	$\Delta z$	$\sigma z$
O <sub>1</sub>	-3	3	3	5	-5	2
O <sub>2</sub>	6	2	5	5	3	2
C <sub>1</sub>	2	4	2	7	-1	3
C <sub>2</sub>	1	5	-9	8	0	4
C <sub>3</sub>	6	5	-9	8	4	4
C <sub>4</sub>	6	5	-7	9	1	4
C <sub>5</sub>	7	5	4	9	-1	4
C <sub>6</sub>	3	4	9	8	-5	3
C <sub>7</sub>	4	4	11	7	-2	3
H <sub>2</sub>	0	30	-14	50	2	30
H <sub>2</sub> '	-3	30	-10	40	-4	20
H <sub>3</sub>	9	30	-5	50	6	30
H <sub>3</sub> '	5	30	-18	40	5	20
H <sub>4</sub>	1	30	-13	40	-2	20
H <sub>4</sub> '	9	30	-9	50	4	30
H <sub>5</sub>	7	30	5	50	-3	30
H <sub>5</sub> '	11	30	9	50	1	30
H <sub>6</sub>	-1	30	4	50	-8	30
H <sub>6</sub> '	4	30	17	50	-7	20
H <sub>7</sub>	9	20	14	30	0	10
H <sub>7</sub> '	3	30	17	60	-5	30

Table 13. Interatomic distances and angles before and after correcting for librational effects, and their estimated standard deviations (Fig. 3).

Bond	Uncorr. (Å)	Corr. (Å)	$\sigma$ (Å)
O <sub>2</sub> -O <sub>3</sub>	1.468	1.472	0.003
O <sub>1</sub> -C <sub>1</sub>	1.437	1.443	0.004
O <sub>2</sub> -C <sub>1</sub>	1.434	1.439	0.004
C <sub>1</sub> -C <sub>2</sub>	1.536	1.542	0.006
C <sub>2</sub> -C <sub>3</sub>	1.515	1.517	0.006
C <sub>3</sub> -C <sub>4</sub>	1.517	1.522	0.006
C <sub>4</sub> -C <sub>5</sub>	1.526	1.534	0.008
C <sub>5</sub> -C <sub>6</sub>	1.525	1.528	0.006
C <sub>6</sub> -C <sub>7</sub>	1.532	1.538	0.005
C <sub>7</sub> -C <sub>1</sub>	1.523	1.529	0.007
C <sub>2</sub> -H <sub>2</sub>		1.03	0.03
C <sub>2</sub> -H <sub>2</sub> '		0.98	0.02
C <sub>3</sub> -H <sub>3</sub>		1.18	0.03
C <sub>3</sub> -H <sub>3</sub> '		1.07	0.03
C <sub>4</sub> -H <sub>4</sub>		1.05	0.03
C <sub>4</sub> -H <sub>4</sub> '		0.97	0.03
C <sub>5</sub> -H <sub>5</sub>		1.09	0.03
C <sub>5</sub> -H <sub>5</sub> '		1.12	0.03
C <sub>6</sub> -H <sub>6</sub>		1.11	0.03
C <sub>6</sub> -H <sub>6</sub> '		0.99	0.03
C <sub>7</sub> -H <sub>7</sub>		1.10	0.02
C <sub>7</sub> -H <sub>7</sub> '		1.00	0.03

Table 13. Continued.

Angle	Uncorr. (°)	Corr. (°)	$\sigma$ (°)
O <sub>3</sub> -O <sub>2</sub> -C <sub>1</sub>	107.8	107.6	0.2
O <sub>4</sub> -O <sub>1</sub> -C <sub>1</sub>	108.4	108.3	0.2
O <sub>1</sub> -C <sub>1</sub> -O <sub>2</sub>	107.8	108.0	0.3
O <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub>	103.8	103.7	0.3
O <sub>2</sub> -C <sub>1</sub> -C <sub>2</sub>	102.9	102.7	0.3
O <sub>1</sub> -C <sub>1</sub> -C <sub>7</sub>	111.4	111.3	0.3
O <sub>2</sub> -C <sub>1</sub> -C <sub>7</sub>	112.9	112.9	0.3
C <sub>7</sub> -C <sub>1</sub> -C <sub>2</sub>	117.2	117.4	0.3
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	117.2	117.0	0.4
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	114.6	114.5	0.4
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	116.5	116.6	0.3
C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	114.2	114.2	0.4
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	113.6	113.5	0.3
C <sub>6</sub> -C <sub>7</sub> -C <sub>1</sub>	113.9	113.8	0.3
Angle		Corr. (°)	$\sigma$ (°)
C <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub>		108	2
C <sub>1</sub> -C <sub>2</sub> -H <sub>2</sub> '		110	2
H <sub>2</sub> -C <sub>2</sub> -H <sub>2</sub> '		103	2
H <sub>2</sub> -C <sub>2</sub> -C <sub>3</sub>		113	2
H <sub>2</sub> '-C <sub>2</sub> -C <sub>3</sub>		105	1
C <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub>		102	1
C <sub>2</sub> -C <sub>3</sub> -H <sub>3</sub> '		109	1
H <sub>3</sub> -C <sub>3</sub> -H <sub>3</sub> '		102	2
H <sub>3</sub> -C <sub>3</sub> -C <sub>4</sub>		114	1
H <sub>3</sub> '-C <sub>3</sub> -C <sub>4</sub>		113	1
C <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub>		107	1
C <sub>3</sub> -C <sub>4</sub> -H <sub>4</sub> '		112	2
H <sub>4</sub> -C <sub>4</sub> -H <sub>4</sub> '		101	2
H <sub>4</sub> -C <sub>4</sub> -C <sub>5</sub>		110	2
H <sub>4</sub> '-C <sub>4</sub> -C <sub>5</sub>		109	2
C <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub>		109	2
C <sub>4</sub> -C <sub>5</sub> -H <sub>5</sub> '		112	2
H <sub>5</sub> -C <sub>5</sub> -H <sub>5</sub> '		114	2
H <sub>5</sub> -C <sub>5</sub> -C <sub>6</sub>		104	2
H <sub>5</sub> '-C <sub>5</sub> -C <sub>6</sub>		104	1
C <sub>5</sub> -C <sub>6</sub> -H <sub>6</sub>		108	1
C <sub>5</sub> -C <sub>6</sub> -H <sub>6</sub> '		112	1
H <sub>6</sub> -C <sub>6</sub> -H <sub>6</sub> '		110	2
H <sub>6</sub> -C <sub>6</sub> -C <sub>7</sub>		104	1
H <sub>6</sub> '-C <sub>6</sub> -C <sub>7</sub>		109	1
C <sub>6</sub> -C <sub>7</sub> -H <sub>7</sub>		114	1
C <sub>6</sub> -C <sub>7</sub> -H <sub>7</sub> '		108	2
H <sub>7</sub> -C <sub>7</sub> -H <sub>7</sub> '		109	2
H <sub>7</sub> -C <sub>7</sub> -C <sub>1</sub>		102	1
H <sub>7</sub> '-C <sub>7</sub> -C <sub>1</sub>		110	2

The agreement between atomic vibration tensor components derived from the least squares refinement, and those calculated from the rigid-body parameters (Table 10), supports the assumption of regarding the molecule as an oscillating rigid body. While the translational motion is approximately isotropic (Table 11), the  $\omega$  tensor implies anisotropic angular oscillation. The

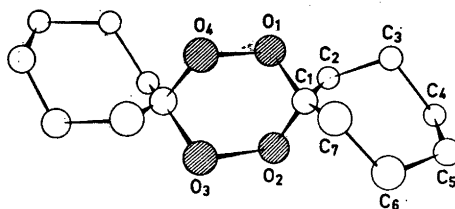


Fig. 3. Schematical drawing of the molecule.

largest r.m.s. amplitude is obtained about an axis nearly parallel to L which corresponds to the smallest moment of inertia.

The corrections in fractional coordinates for librational effects may be found in Table 12.

### DISCUSSION

Referring to Fig. 3, the interatomic distances and angles, before and after correcting for librational effects, are listed in Table 13. Standard deviations in bond lengths and angles were calculated from the standard deviations given in Tables 4 and 6 without taking into account the E.S.D.'s of the cell parameters.

The distances and angles of the tetraoxacyclohexane ring are, within probable limits of error, equal to those found in dimeric cyclohexanone peroxide.<sup>2</sup> The kind of asymmetry around the spiro carbon atom, C<sub>1</sub>, resembles what was observed for dimeric cyclohexanone peroxide, and may thus roughly be described as a "rotation" (*ca.* 4°) about an axis through C<sub>1</sub> approximately normal to the plane defined by C<sub>1</sub>, C<sub>2</sub>, and C<sub>7</sub>. As for the peroxide of cyclohexanone, it appears probable that the distortion is caused by *intramolecular* hydrogen-oxygen repulsions.

The conformation of the cycloheptylidene ring corresponds to what Hendrickson<sup>3</sup> for cycloheptane has called the chair form. The only structure determination reported of a molecule containing a seven-membered ring of this type is the structure of dextrorotary 4-bromo-6,10-dimethylbicyclo[5,3,0]-decane-3-one.<sup>15</sup> Also in this molecule the chair form is the preferred conformation.

From Table 13 it may be seen that the C—C—C angles are greater than in paraffin-chain molecules, the average value being 115.3°. The dihedral angles are:

Angles	$\omega^*$	(°)
C <sub>7</sub> —C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub>	$\omega_4$	24.9
C <sub>1</sub> —C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub>	$\omega_5$	-79.5
C <sub>2</sub> —C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub>	$\omega_6$	105.4
C <sub>3</sub> —C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub>	$\omega_7$	-55.6
C <sub>4</sub> —C <sub>5</sub> —C <sub>6</sub> —C <sub>7</sub>	$\omega_1$	69.6
C <sub>5</sub> —C <sub>6</sub> —C <sub>7</sub> —C <sub>1</sub>	$\omega_2$	-90.8
C <sub>6</sub> —C <sub>7</sub> —C <sub>1</sub> —C <sub>2</sub>	$\omega_3$	49.8

\* Notation of Hendrickson.

The two best least squares planes gave the following fit:

Atoms defining the plane	Deviations (Å)
C <sub>1</sub>	-0.119
C <sub>2</sub>	0.119
C <sub>3</sub>	-0.061
C <sub>7</sub>	0.061
C <sub>3</sub>	-0.071
C <sub>4</sub>	0.083
C <sub>5</sub>	-0.082
C <sub>7</sub>	0.071

Some of the *intramolecular* contacts of hydrogen atoms not bonded to the same carbon atom are short:

Distance	Å	$\sigma$ (Å)
H <sub>6</sub> -H <sub>7</sub>	2.20	0.03
H <sub>3</sub> -H <sub>3</sub>	2.24	0.03
H <sub>3</sub> '-H <sub>4</sub>	2.31	0.03
H <sub>5</sub> -H <sub>3</sub>	2.35	0.03
H <sub>5</sub> '-H <sub>7</sub>	2.36	0.03

The shortest *intermolecular* H—H distance is 2.44 Å (calculated with uncorrected coordinates).

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