Crystal and Molecular Structure of 1-Oxa-azulan-2-one. II. A Refinement of the Structure by Low Temperature Technique

By Yoshio SASADA

(Received August 18, 1958)

As a part of the serial investigations of the compounds containing planar seven-membered carbon rings[1-5], the crystal structure of 1-oxa-azulan-2-one was reported in a preceding paper[6]. In that case the great thermal agitation at room temperature did not permit us to give the detailed determination of its crystal structure. The last Fourier projection indicated, moreover, considerably large anisotropic thermal vibrations of some atoms in the molecule. Therefore, it was highly desirable to carry out intensity measurement at low temperature in order to obtain the molecular dimensions with enough accuracy to discuss the molecular structure quantitatively.

Recently Cruickshank has published several papers[7,8] on the method dealing with molecular motions in crystals, which he applied to the cases of naphthalene[9,10] and anthracene[10-12] and compared the molecular vibrations obtained using X-ray data with those from infrared studies. Thus it will also be interesting to examine the thermal vibration of this polar molecule in order to make comparison with naphthalene and anthracene.

For these two main objects, the study of the crystal structure at low temperature was attempted and the present account deals with the analysis of this compound at $-110°C$.

Apparatus.—For several years, low temperature single crystal diffraction techniques have been adopted by several authors[13]. There are two main distinct procedures: one is the cold gas flow and the other the conduction method. The latter method has the advantage that good constancy of temperature is attained. However, for the present purpose, the former procedure is sufficient because fluctuation of temperature less than 5°C is allowable throughout the experiment.

The apparatus used for this work is shown in Fig. 1. This is a modification of the device described by J. H. Robertson. A large Dewar-vessel, 4 liters in volume, is fitted with a wooden cap in which there are holes for a large tube for filling, a level indicator, a vacuum jacketed nozzle and a pair of wires containing the heating element. Careful regulation of the current in this heating element allows sufficiently constant temperature to be maintained. The leakage of cold nitrogen gas, which make precise temperature control impossible, is avoided by the use of rubber packing.

The cold nitrogen stream is directed at the crystal on the goniometer head of a Weissenberg camera. A thermocouple fixed at the tip of the slit was placed between the tip of the nozzle and the crystal, the distance from the crystal being 3 mm. Difference between temperatures at this position and at the crystal was found to be less than 5°C at $-110°C$.

Special care was taken to prevent the frost from condensing on the crystal itself. For this purpose the cold nitrogen stream is surrounded by a supplementary stream of dry nitrogen gas of about 5°C. The velocity of the latter is controlled so as to reduce the frosting. When kept at $-110°C$, 0.7 litre of liquid nitrogen is necessary for one hour.

Experimental

Preliminary tests were made at 0°C, $-45°C$ and $-110°C$. The cell dimensions at these three temperatures show no sign of discontinuous change of considerable magnitude, the values being as follows: $a=21.4_5$, $b=8.28$, at 0°C; $a=21.3_7$, $b=8.28_5$, at $-45°C$; $a=21.2_6$, $b=8.28_5$Å, at $-110°C$. These values were obtained from the reflexions of (20, 0, 0) and (0, 8, 0) recorded on the same film respectively.

The intensity of each reflexion increases continuously with lowering temperature and the change of intensity is more significant with increasing angles. This corresponds to reduction of thermal motion without any phase transitions.

From these preliminary tests, it was expected that a satisfactory result for the present purpose could be obtained from an experiment at $-110°C$.

The final cell dimensions at $-110°C$ and space

1) Y. Sasada and I. Nitta, *Acta Cryst.*, **9**, 205 (1956).
2) Y. Sasada and I. Nitta, This Bulletin, **30**, 62 (1957).
3) K. Furukawa, Y. Sasada and T. Watanabé, to be published.
4) C. Tamura, Y. Sasada and I. Nitta, to be published.
5) Y. Takaki, Y. Sasada and I. Nitta, to be published.
6) Y. Sasada, This Bulletin, **32**, 165 (1959).
7) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).
8) D. W. J. Cruickshank, ibid., **9**, 747 (1956).
9) D. W. J. Cruickshank, ibid., **10**, 504 (1957).
10) D. W. J. Cruickshank, ibid., **9**, 1005 (1956).
11) D. W. J. Cruickshank, ibid., **9**, 915 (1956).
12) D. W. J. Cruickshank, ibid., **10**, 470 (1957).
13) W. N. Lipscomb, *Norelco Rep.*, **4**, 54 (1957).

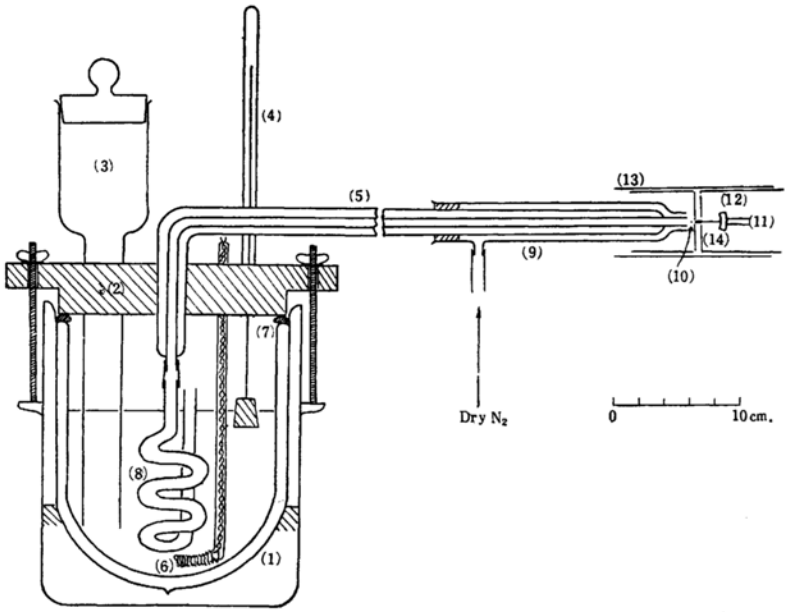


Fig. 1. Cooling apparatus.
(1) Dewar bottle. (2) Wooden cap. (3) Tube for filling. (4) Level indicator. (5) Vacuum jacketed nozzle. (6) Heating coil. (7) Rubber packing. (8) Copper tube. (9) Supplementary nozzle for dry nitrogen. (10) Thermocouple junction. (11) Goniometer head. (12) Screen. (13) Film pack. (14) Crystal.

group are: $a=21.26\pm0.06$, $b=8.28_5\pm0.04$, $c=3.91\pm0.03$Å and $P2_12_12_1$-D_2^4.

Using Cu K_α radiation, three complete sets of relative intensities for ($hk0$) were obtained by the Weissenberg procedure. Throughout the experiment temperature was kept within the range of ±5°C. The specimens used have the following maximum and minimum dimensions at right angle to the axis of rotation: crystal 1, 0.005×0.023; crystal 2, 0.004×0.018; crystal 3, 0.005×0.020 cm.

Intensities were estimated by visual comparison with a scale, which was prepared by counting the number of times of the repeating reflexion of the crystal 3. The multiple-film technique was used to correlate strong and weak reflexions, ranging in relative intensities from 25000 to 1. The corrections for polarization and Lorentz factors were made in the usual way. The effect due to the shape of the specimen was also allowed for.

The values of structure factors used in the following analysis are the weighted means of the values in the above mentioned three sets. Reflexions from 188 planes were observed out of 229 possible ($hk0$)'s.

Results

Refinement of the (001) Projection and Location of the Hydrogen Atoms. — The structure factors observed at -110°C almost agreed with those observed at room temperature, if the mean temperature factor of 4.0×10^{-16}cm^2 was applied to the former. This implies that the structure at low temperature remains essentially the same as that of room temperature so that the refinement can be made starting from the coordinates reported in the preceding paper[6].

Two successive Fourier and an (F_o-F_c) syntheses on the (001) plane were applied to correct the atomic coordinates. The corrections were estimated from the equation

$$\Delta r=(\mathrm{d}(\rho_o-\rho_c)/\mathrm{d}r)_{r=0}/2p\rho(0)$$

where $\rho(0)$ is the electron density at an atomic centre and p is a constant, whose value was deduced from the second Fourier map assuming the electron density near an atomic centre to be represented by the equation

$$\rho(r)=\rho(0)\ \exp(-pr^2)$$

In the structure-factor calculation, the atomic scattering factors were taken from McWeeny[14], using for oxygen $\overline{f}_o=\frac{1}{3}\times(f^{\parallel}+2f^{\perp})$, and for carbon the values for 'valence states'.

It was observed from the $(\rho_o-\rho_c)$ map that the magnitudes of thermal motions of individual atoms are different from each other and some of them are considerably anisotropic. These thermal

14) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

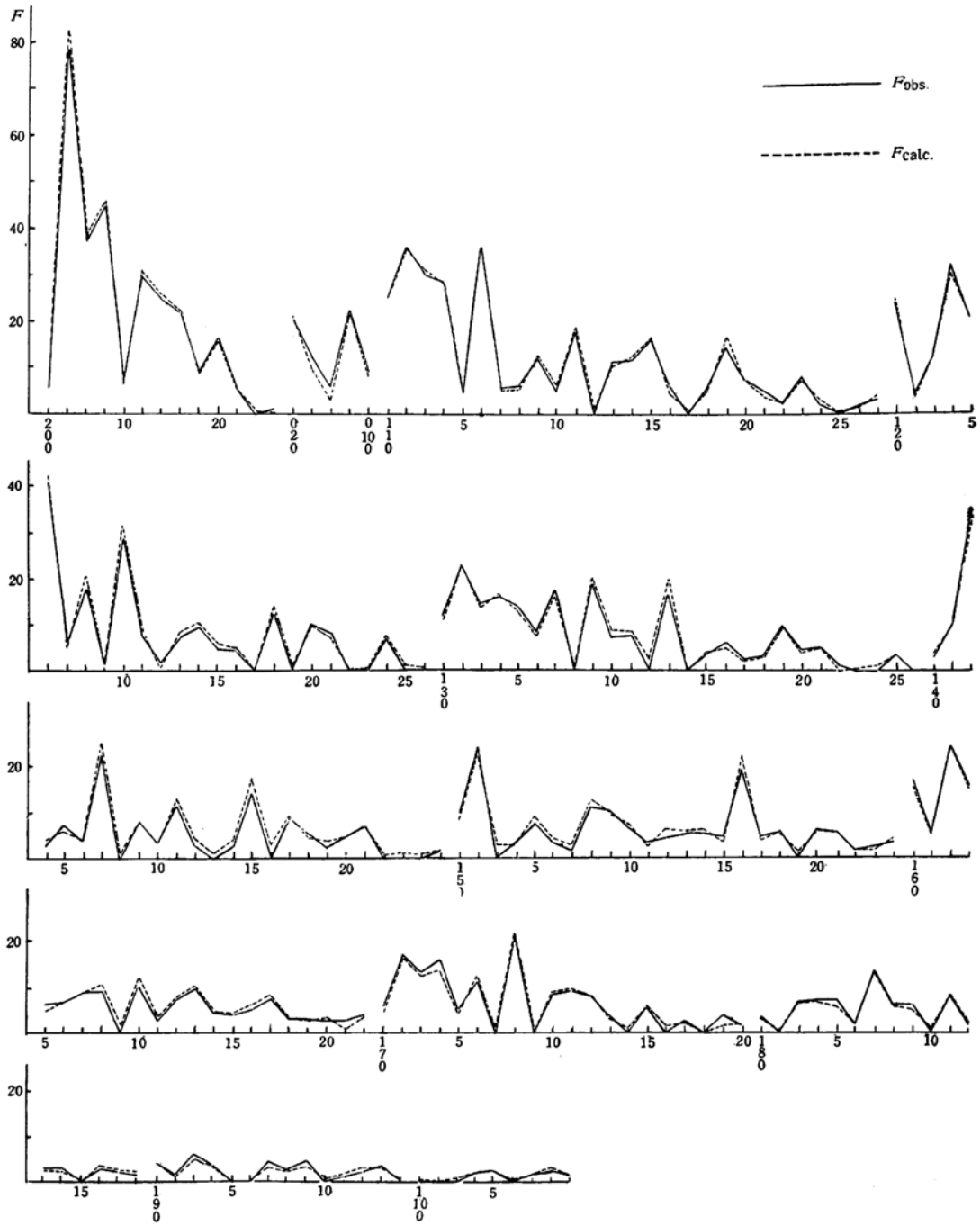


Fig. 2. Observed and calculated structure factors, $F(hk0)$.

factors for individual atoms and their anisotropy were obtained from the successive three (F_o-F_c) syntheses in the following way. The corrections for thermal factors were estimated from the equation[15]

$$\Delta B=\pi^2(\mathrm{d}^2(\rho_o-\rho_c)/\mathrm{d}r^2)_{r=0}/p^2\rho(0)$$

For the atoms vibrating anisotropically, the scattering factors of the form

$$f=f_0\exp[-\{\alpha+\beta\sin^2(\phi-\psi_b)\}(\sin\theta/\lambda)^2]$$

were employed[16,17], where α and β are

15) Y. Sasada, to be published.

16) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
17) W. Cochran, *Acta Cryst.*, **4**, 81 (1951).

constants, ψ_b is the angle between the direction of maximum vibration and the b axis, and $(2\sin\theta, \phi)$ are the polar coordinates of a point in the $(hk0)$ section of the reciprocal lattice, measured from the a^* axis. In the projection it should be noted that only two molecules are equivalent in dealing with the anisotropic vibrations.

Throughout these refinements F_c included the contributions from hydrogen atoms placed radially at a distance of 1.0 Å from the carbon atoms. In Table I are listed the final atomic coordinates and the final thermal parameters. The comparison between observed and calculated structure factors is shown in Fig. 2, where the R index becomes 0.097.

TABLE I
ATOMIC COORDINATES AND THERMAL FACTORS
(AT −110°C)

Atom	x/a	y/b	z/c	α	β	ψ_b
O_1	0.099_5	0.554	0.218	2.3	0.5	97°
O_2	0.168	0.722	0.470	2.6	1.3	87
C_2	0.157	0.589	0.344	2.8	0.5	90
C_3	0.194	0.451	0.319	2.8	0.5	85
C_4	0.180	0.169	0.110	2.3	0.5	95
C_5	0.145_5	0.050	−0.034	2.3	1.7	92
C_6	0.084_5	0.052	−0.160	2.6	1.4	83
C_7	0.042	0.175	−0.168	3.3	0	—
C_8	0.049	0.336	−0.043	2.8	0	—
C_9	0.100_5	0.398	0.115	2.2	0	—
C_{10}	0.162	0.329	0.168	2.2	0	—

Figs. 3 and 4 show the final Fourier projection on the (001) plane and the fifth $(\rho_o-\rho_c)$ map respectively. In the calculation of the latter, F_c's do not include the contributions from the hydrogen atoms. The significant peaks on this map are evidently due to the hydrogen atoms.

Coordinates and Molecular Dimensions. —The x and y coordinates obtained by the low temperature refinement hardly differ at all from those at room temperature. The z coordinates, the changes of which have scarcely any influence on the intra- and intermolecular distances due to the short c period, were expected to show no significant differences with those at room temperature. In fact, the change of the c period is of the same order as that of the a axis and a few oscillation photographs at low temperature did not show essential differences. Therefore the same z coordinates as those at room temperature are used in the following discussions. The final coordinates of the carbon and oxygen atoms are shown in Table I.

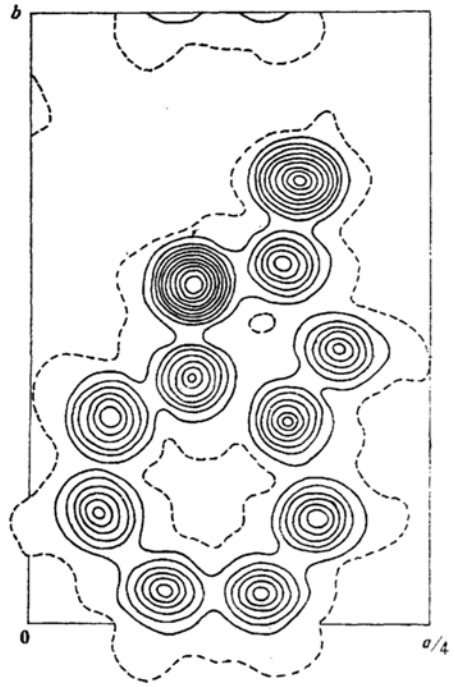


Fig. 3. The final Fourier projection of the electron density on (001). Contours at intervals of 1 e. Å^{-2}. Contour at 1 e. A^{-2} is broken.

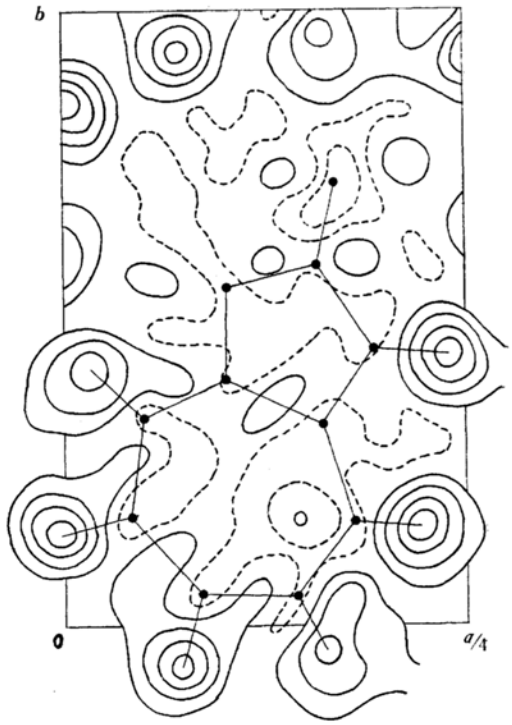


Fig. 4. The final $(\rho_o-\rho_c)$ projection on (001). Contours at intervals of 0.2 e. Å^{-2}. The zero and negative contours are broken.

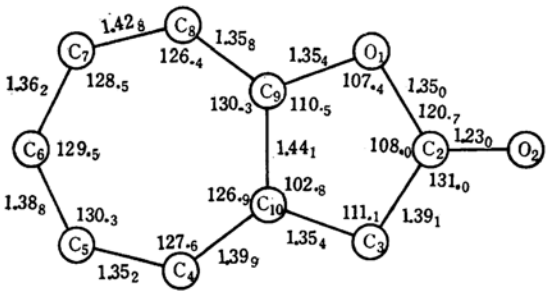
By the use of least squares method the best plane through all carbon and oxygen atoms in the fused ring was determined to be

$$z=0.3634x+0.3192y-1.4186$$

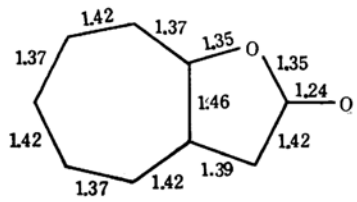
The perpendicular displacements of individual atoms from this mean plane are shown in Table II. The average displacement is 0.02$_4$ Å. The bond lengths and valency angles in the molecule are shown in Fig. 5 (a).

TABLE II
THE PERPENDICULAR DISPLACEMENT OF THE ATOMS FROM THE MEAN PLANE

Atom	Displacement (Å)
O_1	+0.033
O_2	+0.044
C_2	−0.007
C_3	−0.023
C_4	+0.010
C_5	+0.027
C_6	+0.002
C_7	−0.023
C_8	−0.015
C_9	+0.036
C_{10}	−0.042



(a)



(b)

Fig. 5. (a) Observed bond lengths (Å) and bond angles (°). (b) Bond lengths calculated by Pauling's relation.

The estimated positions of hydrogen atoms from the fifth ($\rho_o-\rho_c$) map are given in Table III, the z coordinates being obtained by substituting the estimated x and y values in the equation of the mean plane of the molecule, although the assumed positions were used in the calculations of the ($hk0$) structure factors.

TABLE III
HYDROGEN COORDINATES AND BOND LENGTHS OF C—H

Atom	x(Å)	y(Å)	z(Å)
H_3	5.14	3.62	1.61
H_4	4.72	1.33	0.72
H_5	3.40	−0.31	−0.28
H_6	1.53	−0.58	−1.05
H_7	0.04	1.22	−1.02
H_8	0.36	3.46	−0.18

C_3—H_3=1.09, C_4—H_4=0.94, C_5—H_5=0.80,
C_6—H_6=1.13, C_7—H_7=0.95, C_8—H_8=0.91 Å

Estimation of Accuracy.—The standard deviations of the atomic coordinates, $\sigma(x)$ and $\sigma(y)$ were estimated by the method of Cruickshank[18-20] as follows: $\sigma(x)$= 0.010−0.012; $\sigma(y)$=0.007−0.009 Å for carbon; $\sigma(x)$=0.007−0.008; $\sigma(y)$=0.005 Å for oxygen.

If the small error introduced by the uncertainty of the molecular orientation is ignored, the standard deviation of a bond length can be shown, in this case, to be

$$\sigma(b)=\sigma(d)\times b/d$$

where b is the length of the bond and d is its length in the projection on (001). From this equation the standard deviation of a C—C bond comes out to be about 0.018Å, and that of a C—O bond about 0.012 Å. The average standard deviation of bond angles was found to be 0.7°, and the standard deviation of electron density was 0.18 e. Å^{-2} for the (001) projection.

Discussion

Molecular Structure. — It is recognized clearly from Fig. 5 (a) that a larger and a

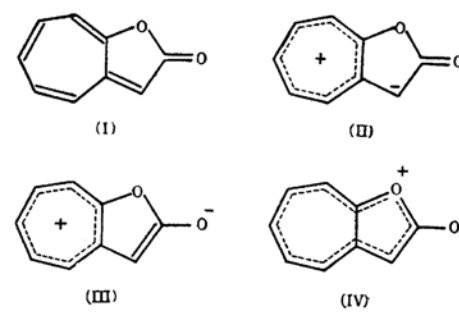


Fig. 6. Canonical formulae.

18) D. W. J. Cruickshank, ibid., **2**, 65 (1949).
19) D. W. J. Cruickshank, ibid., **7**, 519 (1954).
20) F. R. Ahmed and D. W. J. Cruickshank, ibid., **6**, 385 (1953).

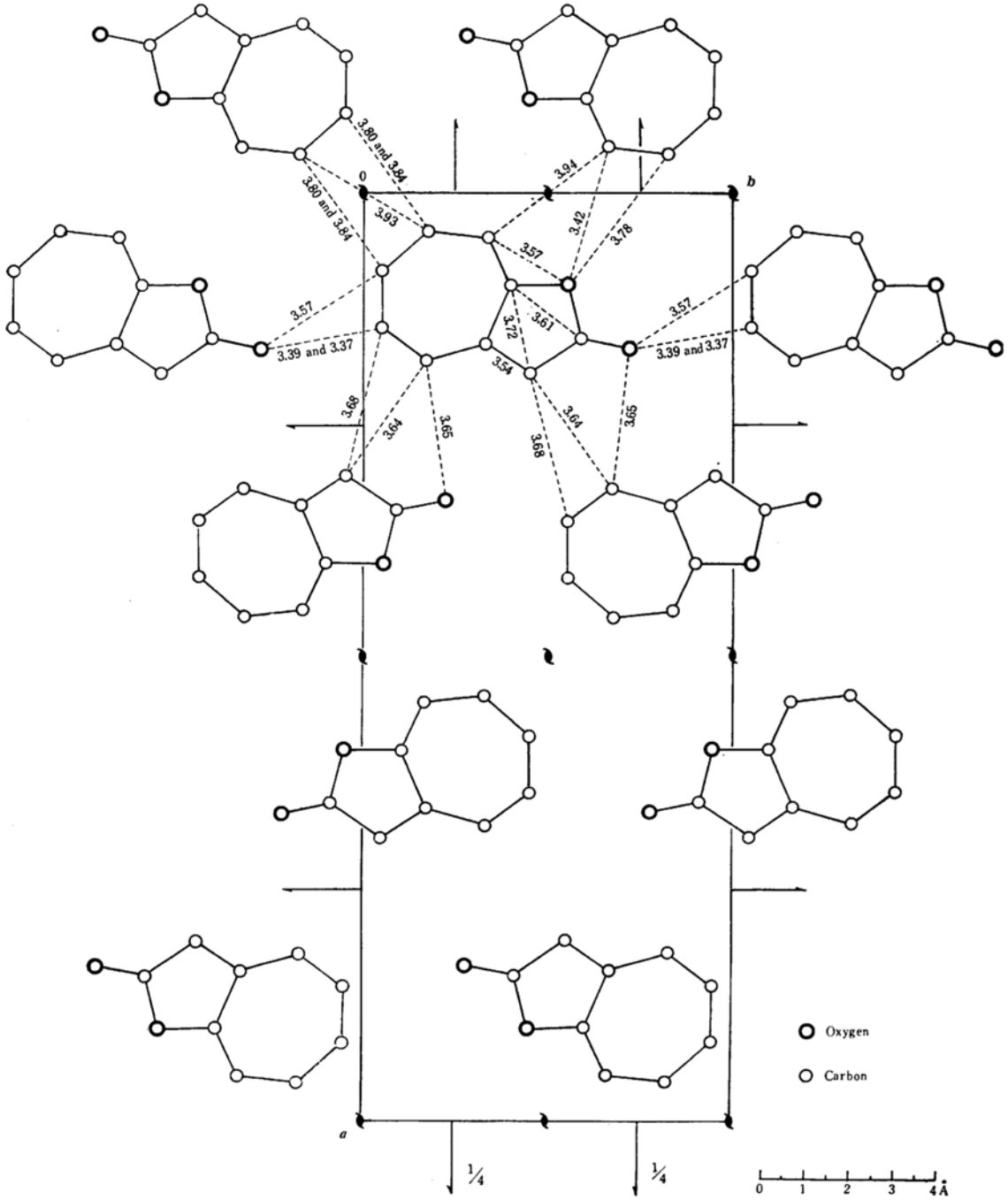


Fig. 7. Arrangement of molecules in the (001) projection with intermolecular distances (Å).

shorter C—C bonds are disposed alternately. The mean values for the larger and shorter C—C bonds are 1.40_9 and 1.35_7Å with estimated standard deviations of 0.01_0 Å respectively. The difference between these two values is highly significant, and this fact favors the conventional chemical formula I shown in Fig. 6.

However, the mean value of the larger C—C bonds and that of two C—O bonds in the five-membered ring (with standard deviation of 0.01_0 Å) are significantly different from their pure single bond lengths respectively. Thus, in order to interpret the bond distances more quantitatively, it becomes necessary to take into account the many resonance structures shown in Fig. 6.

In other words this molecule is not a simple γ-lactone but has the contributions from the structures similar to those in azulene and tropolone. As in the case of tropolone, the carbonyl oxygen is responsible for the drawing out of the ring electron and the lone pair electrons of the oxygen atom in 1-position supply the electron to carbonyl oxygen. The best agreement between measured and calculated bond lengths was obtained taking the following contributions: I, 34%; II (seven structures), each 3%; III (seven structures), each 3%; IV (two structures), each 12%, the relation[21]

$$R=R_1-(R_1-R_2)3x/(2x+1)$$

being used with $R_1=1.54$(C—C), $R_2=1.34$ Å (C=C), $R_1=1.42$ (C—O) and $R_2=1.20$ Å (C=O), (Fig. 5 (b)).

Considering the resonance structures given above, it seems that the seven-membered ring itself is somewhat positively charged. This is justified by the large dipole moment of this molecule[22] and by some chemical evidences[23], and also compatible with characteristic molecular arrangement in the crystal described in Part I of this series[6].

Molecular Arrangement. — The crystal structures projected on the (001) and (010)

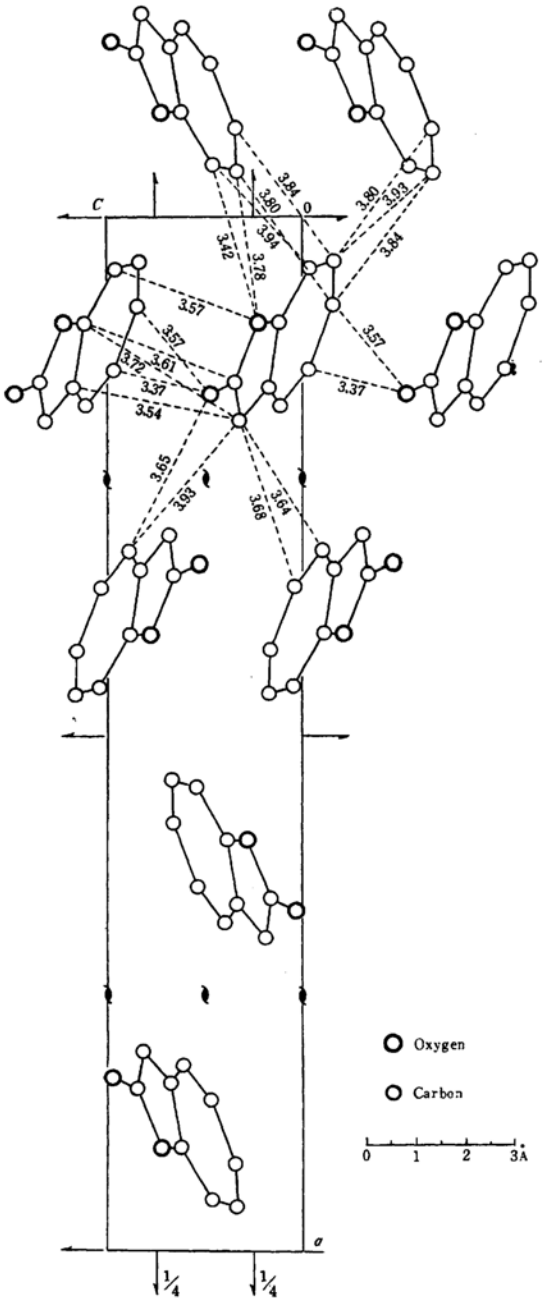


Fig. 8. Arrangement of molecules in the (010) projection with intermolecular distances (Å).

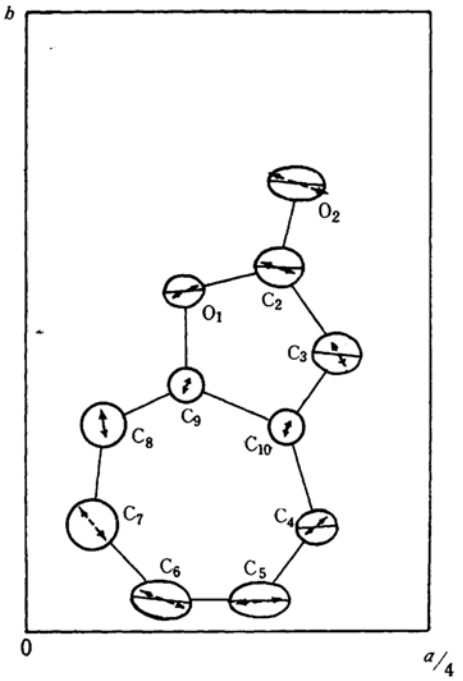


Fig. 9. Anisotropic thermal motions of individual atoms. Dimensions of solid circles and ellipses are proportional to the r. m. s. amplitudes estimated from B factors. The dotted arrows show the direction and relative magnitudes of the vibration of individual atoms due to the rigid-body angular oscillation of the molecule about its mass centre.

21) L. Pauling, "The Nature of the Chemical Bond", Ithaca, Cornell University Press, (1948).
22) Y. Kurita and M. Kubo, to be published.
23) S. Seto, *Sci. Rep. Tahoku Univ., Ser. I*, **37**, 367 (1953).

planes are shown in Figs. 7 and 8 respectively, together with the intermolecular distances. Intermolecular distances at a low temperature are shorter by about 0.03 Å than those at room temperature. Anisotropy of the change of the intermolecular distances, however, can not be detected owing to the greater standard deviations for them at room temperature.

Although an outline of the crystal structure is the same as that mentioned in Part I, the molecular arrangement can also be described as an assembly of the rods in which the molecules are joined together in a file by the interaction of dipoles in the same directions. The interaction between rods is less than that in the rod.

The thermal expansion coefficient along the *b* axis, which agrees approximately with the direction of the rod, is of negative sign, and those along the *a* and *c* axes are positive and of the same order as those in ordinary organic crystals[24]. This fact can be interpreted well from the point of view mentioned above, and will be further discussed in the following paragraph in connection with the anisotropic thermal vibrations.

Anisotropic Thermal Motion. — Fig. 9 shows the anisotropic thermal vibrations schematically. Dimensions of solid circles and ellipses are proportional to the r.m.s. amplitudes estimated from the *B* factors. These can be understood as the coupling of rigid-body libration of the molecule about its mass centre and the translational vibration whose amplitude along the *a* axis is greatest. The r. m. s. amplitudes of angular oscillation are about 3° and those of the translational vibration along the *a* and *b* axes 0.17 and 0.15 Å respectively. Contrary to the cases of naphthalene[9] and anthracene[11,12], the translational amplitude along the long axis of the molecule is smaller than that along the short axis. This is compatible with the characteristic arrangement of the polar molecules mentioned above.

The present author wishes to express his sincere thanks to Professor I. Nitta for his guidance and encouragement throughout this work. He is also indebted to Professor T. Nozoe for supplying the sample and for his continued interest and to Professor T. Watanabé for his kind advice particularly on the low temperature techniques.

Department of Chemistry, Faculty of Science, Osaka University
Kita-ku, Osaka

24) I. Woodward, *Acta Cryst.*, **11**, 441 (1958).