Crystal and Molecular Structure of 1-Oxa-azulan-2-one. I. X-ray Determination of Crystal Structure

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We investigated previously the crystal and molecular structures of sodium salt[1] and hydrochloride of tropolone[2,3] as a part of the serial structural studies of the compounds containing planar seven-membered carbon rings. We have extended our study to the related compounds of azulene. Azulene, a fused five- and seven-membered ring system, is a well-known representative of non-benzenic aromatic compounds. Since Hückel[4] explained the large dipole moment of this compound by molecular orbital treatment, many theoretical and experimental researches especially measurements of dipole moment and absorption spectra, on azulene and its derivatives have been made. These studies were reviewed by several authors[5]. However, there have appeared only a few investigations using diffraction methods which can determine the molecular structures in detail. Even for the mother substance, azulene, it was in 1956 that its structure was reported by Takeuchi and Pepinsky[6] and Robertson and Shearer[7] independently, but no accurate molecular dimension sufficient to discuss in comparison with the theoretical results has

1) Y. Sasada and I. Nitta, *Acta Cryst.*, **9**, 205 (1956).
2) Y. Sasada, K. Osaki and I. Nitta, ibid., **7**, 113 (1954).
3) Y. Sasada and I. Nitta, This Bulletin, **30**, 62 (1957).
4) E. Hückel, *Z. Physik.*, **70**, 204 (1931).
5) e. g., M. Gordon, *Chem. Rev.*, **50**, 127 (1952).
6) Y. Takeuchi and R. Pepinsky, *Science*, **124**, 126 (1956).
7) J. M. Robertson and H. M. M. Shearer, *Nature*, **172**, 885 (1956).

yet been reported. The other few papers on structures of azulene derivatives[8] deal only with crystal data or approximate structures.

Thus the accurate determination of these compounds by means of X-ray analyses will be desirable to the structural chemistry of non-benzenic aromatic compounds. Moreover, the accumulation of knowledge on the molecular orientation in the crystals so determined may contribute to the crystal chemistry of organic compounds, because, for example, azulene is isomer to naphthalene but the electron density distributions in the molecules are more or less different from each other.

Nozoe and his collaborators[9] have obtained, since several years ago, many related compounds of azulene from corresponding derivatives of tropolone, and they kindly supplied us with their valuable products. We have determined the crystallographic data of these compounds[10], some of which were further analysed[11,12]. The present account deals with the structure determination of 1-oxa-azulan-2-one, together with some remarks on the method of X-ray analysis.

Experimental

Crystals are obtained as very fine yellow needles elongated in the c axis direction.

Crystallographic and physical data obtained are as follows:

1-Oxa-azulan-2-one, $C_9H_6O_2$, m. p. 69~70°C; Orthorhombic; $a=21.45\pm0.08$, $b=8.28\pm0.04$, $c=3.96\pm0.02$ Å; Absent spectra, $(h00)$, $(0k0)$ and $(00l)$ when h, k and l are odd respectively; Space group, $P2_12_12_1-D_2^4$; Four molecules per unit cell; Volume of unit cell, 703 Å^3; Density (by floatation); 1.36 g. cm^{-3}; Density (calc.), 1.38 g. cm^{-3}; Linear absorption coefficient for Cu K_α radiation, $\mu=9.45$ cm^{-1}; Total number of electrons per unit cell, $F(000)=304$.

For the structure analysis, a complete set of relative intensities for $(hk0)$, $(hk1)$ and $(hk2)$ was obtained by the integrated Weissenberg procedure. The specimen used has the following maximum and minimum dimensions at right angles to the axis of rotation: 0.01×0.02 cm.

Intensities were estimated by visual comparison with a calibrated scale. The multiple-film technique was used to correlate strong and weak reflexions, ranging in relative intensities from 22000 to 1. Reflexions from only 128 planes were observed out of 232 possible $(hk0)$'s. The corrections for polarization and Lorentz factors were made in the usual way, and that for absorption was neglected.

Results and Discussion

Structure Determination. — Patterson functions[13] have been customarily used in order to obtain some clues to the structure determination problems. However, the two-dimensional Patterson method is generally powerless in the case of the crystals containing no heavy atoms.

For several years, proposals of the so-called direct methods of crystal analysis[14,15] have been made and some of them were applied with success to the actual structure determinations. However, these successful applications are only for the fortunate cases. Some empirical remarks on this point were made by Watase and Nitta[16]. The cause of the inapplicability is due to the fact that the limiting conditions for deriving these analytical forms, such as the non-negativity principle of electron density, are scarcely severe enough. As the actual situations are more complicated, analytical processes based on such rather simple conditions are not enough to solve the crystal structures containing more than, e. g. five independent atoms in the cell.

Therefore the applications of the systematic methods mentioned above may not be effective for the present case. Otherwise information given by individual intensity of each reflexion had to be used carefully as it is.

The very short period of the c axis suggests that the approximate crystal structure can be obtained by the use of the $(hk0)$ reflexions alone. The starting-point was very favorable; that is, the shape of the molecule was already known from the preceding studies of the related compounds. Moreover, the shortest axis of the unit cell strongly limited the inclination of the molecular plane to the (001) plane.

As the plane group of this projection is pgg, the structure factors are represented as follows:

For the reflexions with $h+k=2n$

$$F(hk0)=\sum_j f_j \cos 2\pi hx_j \cos 2\pi ky_j$$

and for the reflexions with $h+k=2n+1$

8) e. g., K. H. Jost, *Naturwiss.*, **43**, 224 (1956).
9) T. Nozoe, Festschrift Arthur Stoll (Birkhauser A.G.) Basel, p 746 (1957).
10) Y. Sasada, to be published.
11) C. Tamura, Y. Sasada and I. Nitta, to be published.
12) Y. Takaki, Y. Sasada and I. Nitta, to be published.
13) A. L. Patterson, *Z. Krist.*, **90**, 517 (1935).
14) D. Harker and J. S. Kasper, *Acta Cryst.*, **1**, 70 (1948).
15) J. Karle and H. Hauptmann, ibid., **3**, 181 (1950).
16) H. Watase and I. Nitta, This Bulletin, **31**, 714 (1958).

$$F(hk0) = -\sum_j f_j \sin 2\pi hx_j \sin 2\pi ky_j$$

The structure factor maps, graphical representations of the above formulae, were made for all reflexions in the region within $2\sin\theta = 1.2$, the maps being drawn in the scale of 4 cm. = 1 Å.

The planes with very strong or weak intensities in the region with small $2\sin\theta$ severely limit the allowable approximate regions of molecular position and orientation together with symmetry considerations. For example, the value of the unitary structure factor of (400) is 0.36 and that of (200) is very small. As shown in Fig. 1, these facts require that the molecule should be in the regions A or B

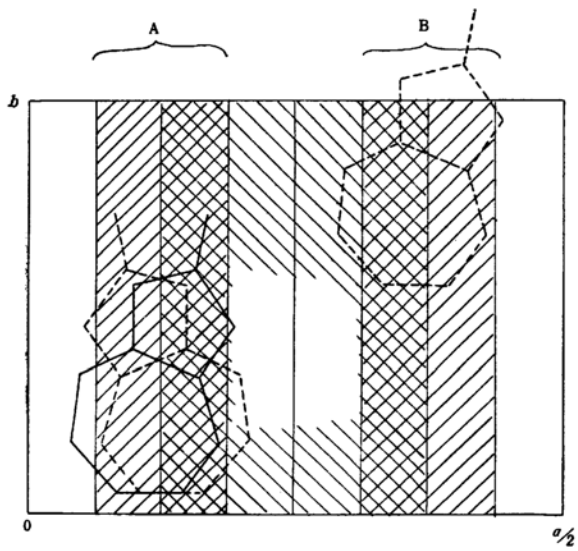

Fig. 1. Example of the determination of the allowable approximate regions using the structure factor maps. The areas shaded with lines obliqued right and left represent the negative regions in the structure factor maps of (400) and (200) respectively.

and the direction of the long axis of the molecule is nearly parallel to the *b* axis. From symmetry considerations, the molecule shown by the dotted line in the region B is equivalent crystallographically to that shown by the dotted line in the region A. Therefore, it was sufficient to apply the trial only to the region A.

The number of possible sets of atomic coordinates in this region which explains the intensities of lower order reflexions was reduced by elimination because of the requirements of the intensities of the higher order reflexions using the structure factor maps. After these successive procedures the structure has been obtained for which the agreement between the observed and the calculated structure factors is fairly good. (After the completion of this structure determination, it was found that the coordinates so obtained deviated from the final positions only by 0.2 Å or less.) Then ordinary Fourier and $(F_o - F_c)$ syntheses followed.

It is noted that the distinction of two structures shown by solid and dotted lines occurs only for the structure factors (*hk*0) with odd *h*. In fact, the structure shown by the dotted line, which was concluded to be false from the detailed trial for (*hk*0) with odd *h*, can also give a Fourier map pretty well to some extent. The detail on this point will be discussed elsewhere.

In the structure-factor calculation, the atomic scattering factors were taken from McWeeny[17], using for oxygen $\overline{f_o} = \frac{1}{3}(f^{\parallel} + 2f^{\perp})$ and for carbon the values for 'valence states'. The corrections were made only for isotropic *B* factors of individual atoms, though it was observed from the $(\rho_o - \rho_c)$ map that thermal motions of some atoms were anisotropic. The best *B* factors were: 6.0 for O_1, C_3, C_4, C_8, C_9 and C_{10}; 7.5 for O_2, C_2, C_5, C_6 and C_7.

The *R* index decreased to 0.134 including the contributions from hydrogen atoms placed radially at a distance of 1.0 Å from the carbon atoms.

TABLE I

ATOMIC COORDINATES (AT ROOM TEMPERATURE)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
O_1	0.100	0.552	0.218
O_2	0.169	0.721	0.470
C_2	0.158	0.588	0.344
C_3	0.194	0.448	0.319
C_4	0.180	0.173	0.110
C_5	0.145	0.051	−0.034
C_6	0.084	0.052	−0.160
C_7	0.042	0.179	−0·168
C_8	0.050	0.335	−0.043
C_9	0.101	0.399	0.115
C_{10}	0.161	0.331	0.168

In Table I are listed the final atomic coordinates. Fig. 2 shows the comparison between observed and calculated structure factors and Fig. 3 the final Fourier projection of the electron density on the (001) plane.

Determination of *z* Coordinates.—As this crystal is a very fine needle in shape, the Weissenberg photographs about the *a* and *b* axes could not be taken. However, the

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

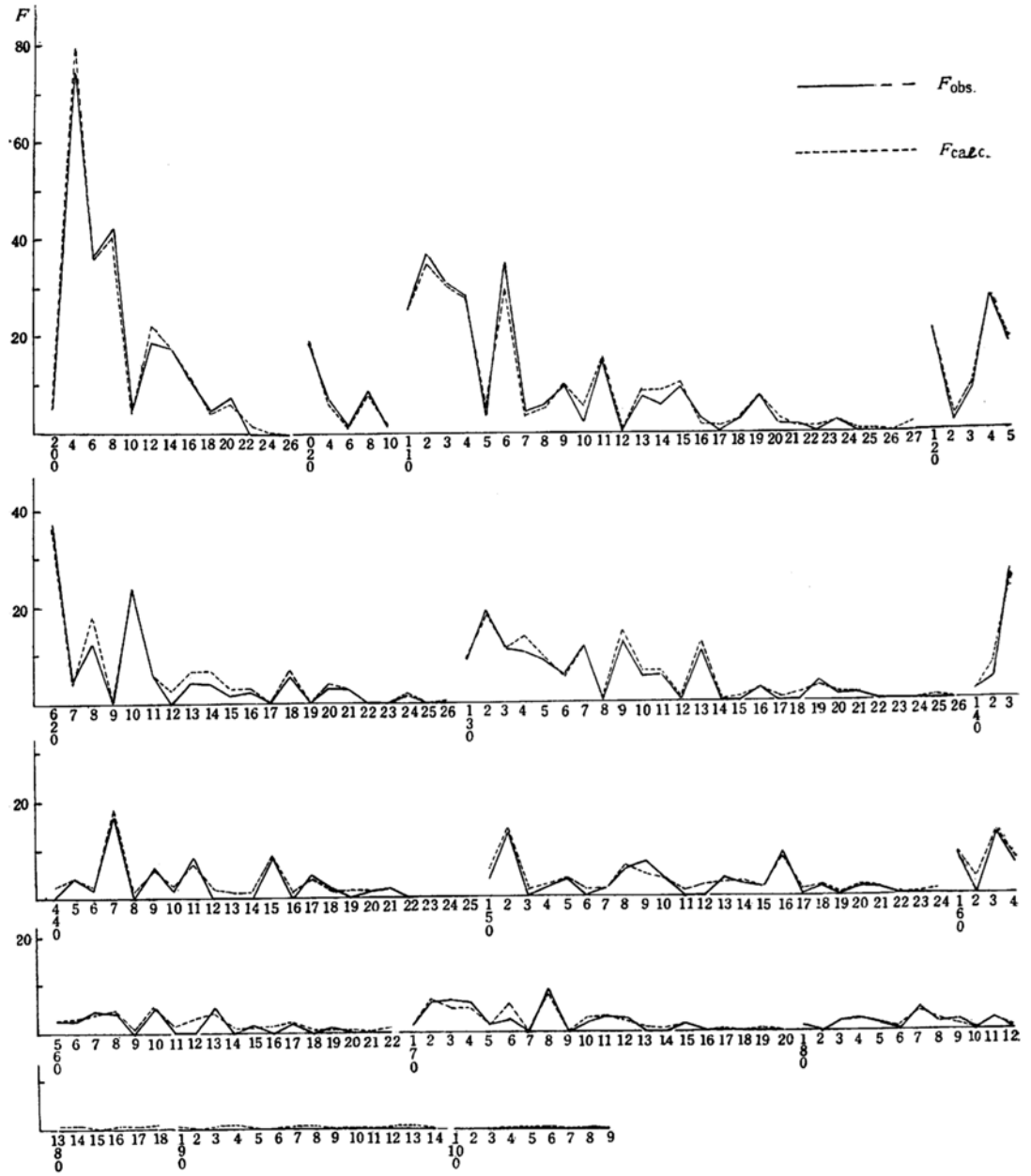

Fig. 2. Observed and calculated structure factors, $F(hk0)$.

very short period of the c axis does not require the full zonal reflexions about the a and b axes in order to estimate z coordinates. The data for $(0kl)$ and $(h0l)$ reflexions were taken from the equi-inclination Weissenberg photographs for the $(hk1)$ and $(hk2)$.

The process of the trial was very simple because the x and y parameters were already known. The coordinates so obtained were refined by the least squares method with suitable weights. For convenience, at the early two cycles, the four parameters, that is, z coordinate of the mass centre of the molecules, angles of the long and short axes of the molecule with the (001) plane and z coordinate of O_2, were corrected assuming the planarity of the fused system of five- and seven-membered rings. In the succeeding two cycles, the z coordinates of eleven atoms were shifted independently.

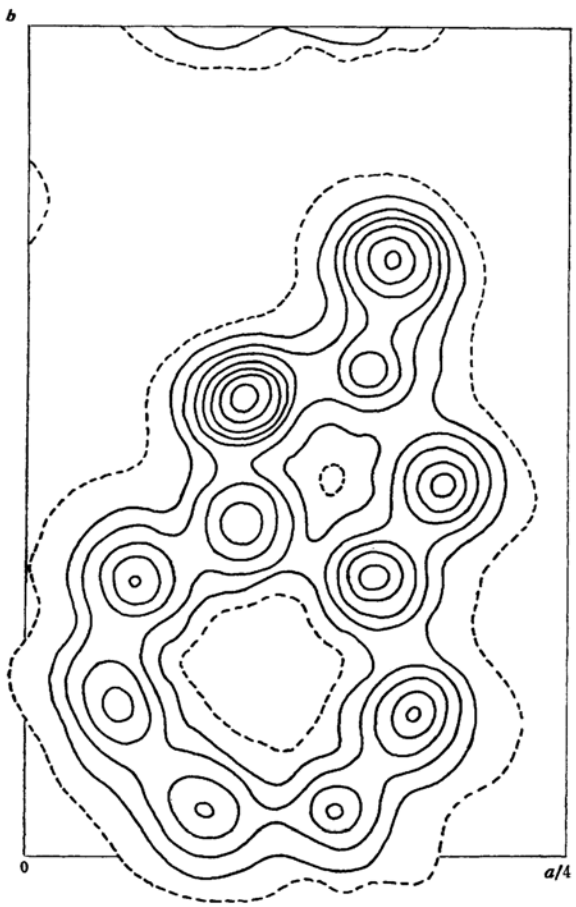

Fig. 3. The final Fourier projection of the electron density on (001). Contours at intervals of 1 e. Å^{-2}. Contour at 1 e. Å^{-2} is broken.

The final z coordinates are listed in Table I and the comparison between observed and calculated structure factors in Fig. 4.

Description of the Structure.—Fig. 5 shows the crystal structure projected on the (001) plane together with intra- and intermolecular distances.

The detailed discussions on the molecular structure are not significant, because the estimated standard deviations of bond lengths reach the values of about 0.04 Å owing to large thermal motions of atoms in the crystal.

There are no intermolecular distances deviating greatly from the sums of normal van der Waals radii.

As seen from Fig. 5, the molecular arrangement is somewhat characteristic. The seven-membered carbon ring, which is supposed to be the electrically positive part of the molecule, has as the first neighbors six five-membered rings, the negative parts, if we include the one within its own molecule. The five-membered ring is also surrounded by six seven-membered rings. Such characteristics of the molecular orientations are in contrast with those of azulene[6,7] and 2-amino azulene[12]. Mutual molecular orientations in these crystals are similar to those in naphthalene[18]. As the basic principles of the packing of molecules in organic crystals are yet to be explored, we shall only point out the parallel relation between molecular orientation and magnitudes of dipole moments of these substances. (According to Kurita and Kubo[19], the values of dipole moments are 5.64, 2.09 and 1.0 D for the present molecule, 2-amino azulene and azulene itself respectively.)

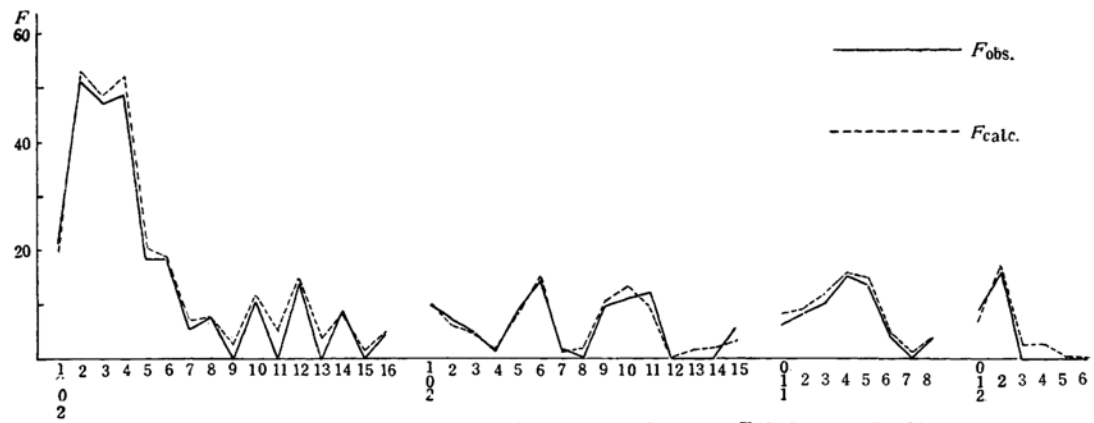

Fig. 4. Observed and calculated structure factors, $F(h0l)$ and $F(0kl)$.

18) S. C. Abrahams, J. M. Robertson and J. G. White, ibid., 2, 238 (1949).

19) Y. Kurita and M. Kubo, to be published.

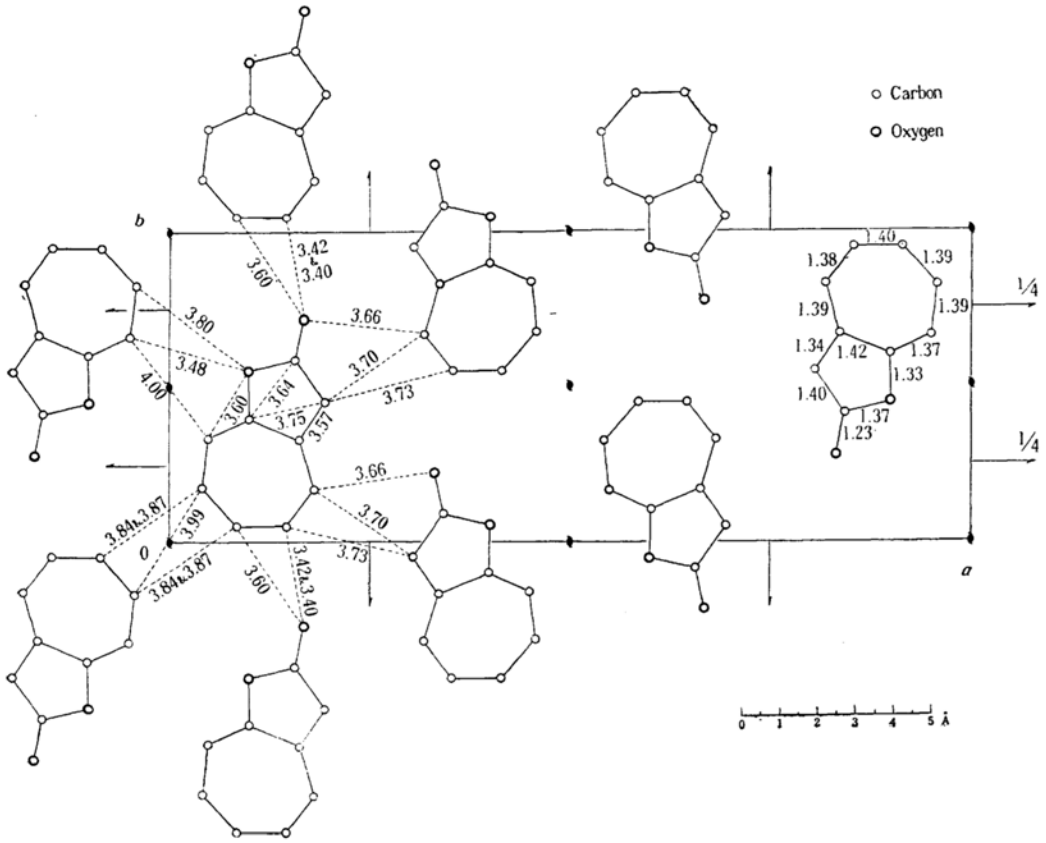

Fig. 5. Crystal structure projected on (001), together with intra- and intermolecular distances (Å).

Finally it was noticed that the *B* factor of each atom increases with increasing distance of an atom from the mass center of the molecule. This may correspond to the oscillational vibration of the molecule about its mass center.

Further discussion on these points will be given in the following paper which describes the refinement of the structure of this substance by low temperature technique.

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