Crystal Structure of 2-Chloro-1-aza-azulene

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We have studied several crystal structures of the molecules containing a seven-membered carbon ring, such as tropolone hydrochloride, sodium tropolonate and 1-oxa-azulan-2-one[1-7]. As a part of these serial investigation, the present account deals with the crystal structure of 2-chloro-1-aza-azulene, which Professor T. Nozoe and his collaborators kindly supplied us.

Experimental

Crystal and physical data obtained are: 2-Chloro-1-aza-azulene, C_9H_6NCl, m.p. 72~73°C. Monoclinic, $a=16.00\pm0.07$, $b=7.50\pm0.04$, $c=7.03\pm0.03$ Å, $\beta=113.8\pm0.5$°C.

Absent spectra; $(h\,0\,l)$ when h is odd, $(0\,k\,0)$ when k is odd. Space group; $P2_1/a-C_{2h}^5$. Four molecules per unit cell. Volume of unit cell; 771.9 $Å^3$. Density (by flotation); 1.40 $g.cm^{-3}$. Density (calculated); 1.41 $g.cm^{-3}$. Linear absorption coefficient for Cu K_α radiation,

$$\mu = 37.5\ cm^{-1}$$

Total number of electrons per unit cell, $F(0\,0\,0)=336$.

Weissenberg photographs were taken at room temperature around the b and c axes, using Cu K_α radiation. The crystals used, which were cut from a large brown block, were square in cross section with rectangular dimensions:

0.05×0.06 cm. for the b axis rotation,

0.06×0.08 cm. for the c axis rotation.

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 8000 to 1 for $(h\,0\,l)$ and from 6000 to 1 for $(h\,k\,0)$ reflexions. Reflexions from 102 and 76 planes were observed out of 135 possible $(h\,0\,l)$'s and 143 $(h\,k\,0)$'s respectively. The corrections for polarization and Lorentz factors were made in the usual way, and that for absorption was omitted.

Results

Structure Determination. — The initial step was intended to locate the chlorine atom by computing Patterson functions $P(uw)$ and $P(uv)$. $P(uw)$ showed three broad peaks, of which two overlapped each other. While the possibility that the one peak is due to the interatomic vector between two chlorines can be excluded by the comparison with $P(uv)$, it was impossible to decide which of the remaining two corresponds to the actual

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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) Y. Sasada, ibid., **32**, 165 (1959).

5) Y. Sasada, ibid., **32**, 171 (1959).

6) Y. Takaki, Y. Sasada and I. Nitta, to be published.

7) K. Furukawa, Y. Sasada and T. Watanabé, to be published.

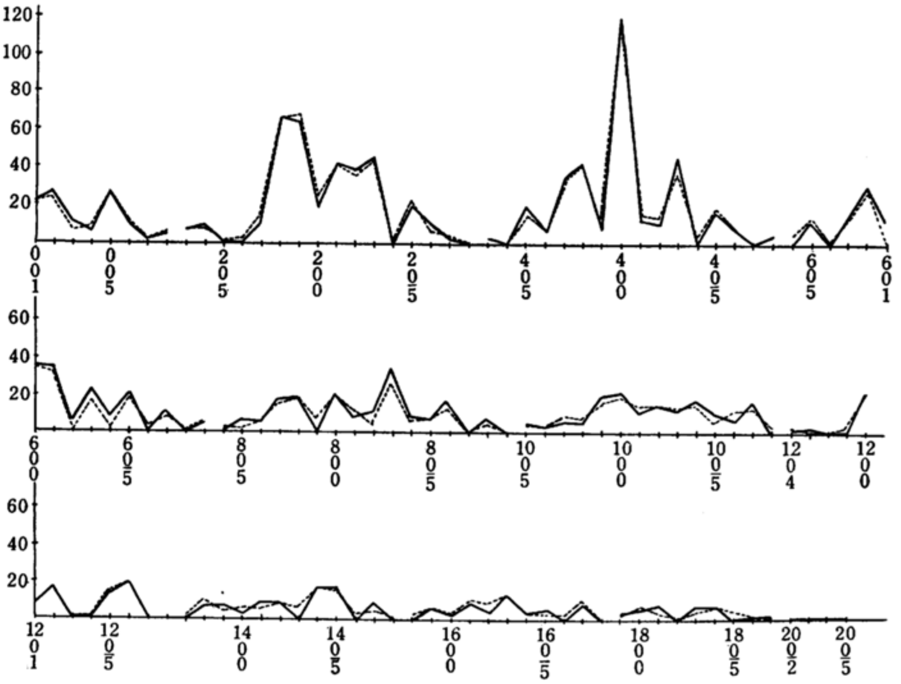

Fig. 1. Observed and calculated structure factors, $F(h\,0\,l)$.

—— $F_{\text{obs.}}$, …… F_{calc}.

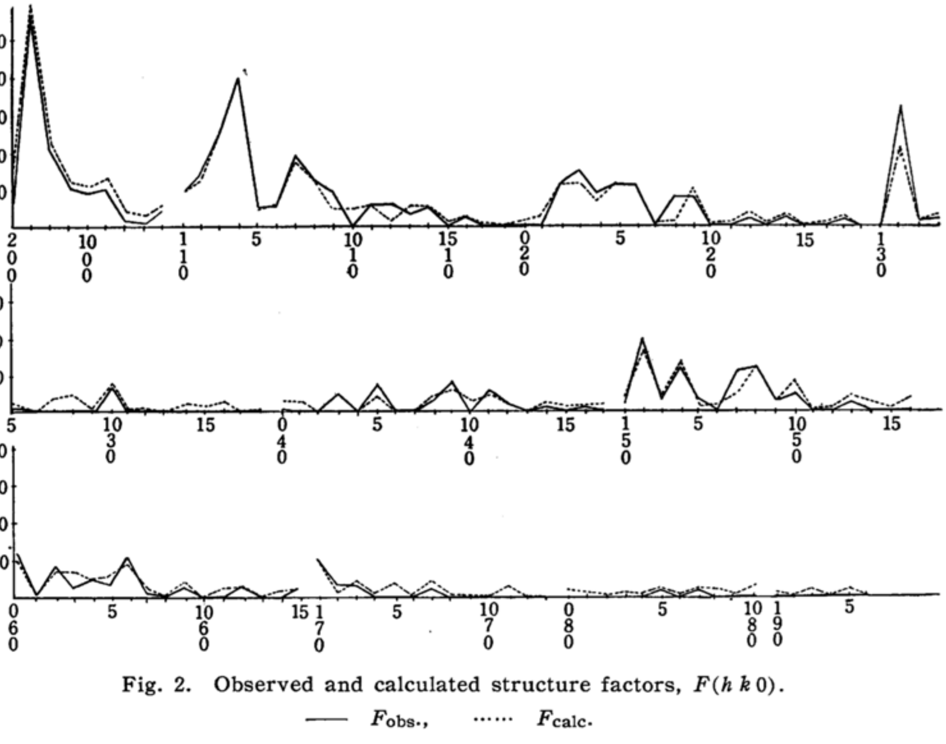

Fig. 2. Observed and calculated structure factors, $F(h\,k\,0)$.

—— $F_{\text{obs.}}$, …… F_{calc}.

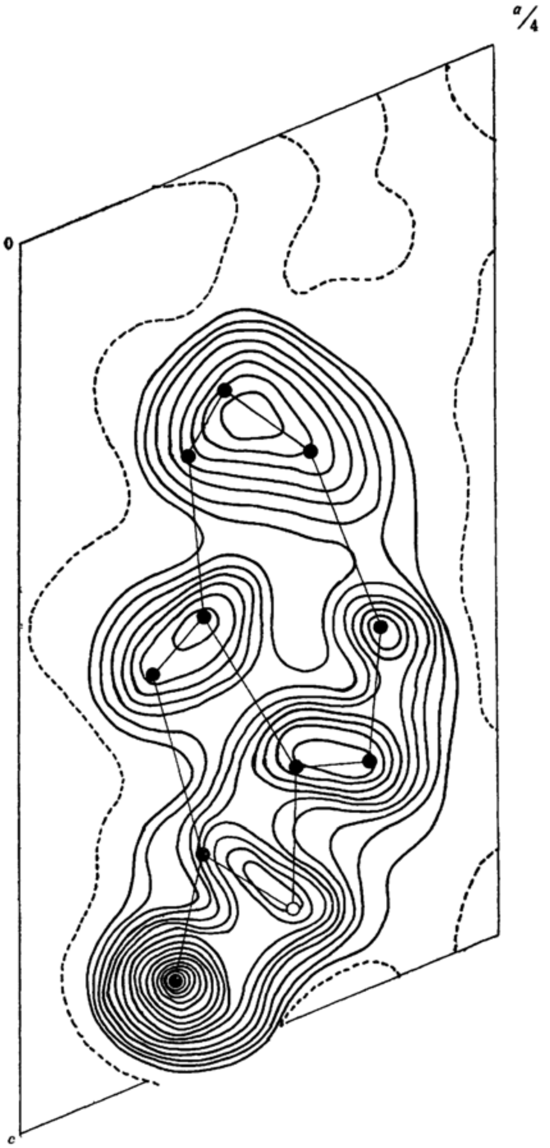

Fig. 3. The final Fourier projection of the electron density along the b axis. Contours at intervals 1 eÅ^{-2}. Contour at 1 eÅ^{-2} is broken.

TABLE I. ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Cl	0.080_5	0.064	0.903
N	0.142	0.401	0.868
C_2	0.097	0.230	0.772
C_3	0.073_5	0.227	0.546
C_4	0.090_5	0.466	0.330
C_5	0.111_5	0.622	0.264
C_6	0.152_5	0.772	0.365
C_7	0.191_5	0.798	0.603
C_8	0.187	0.657	0.758
C_9	0.147	0.494	0.715
C_{10}	0.097	0.390	0.510

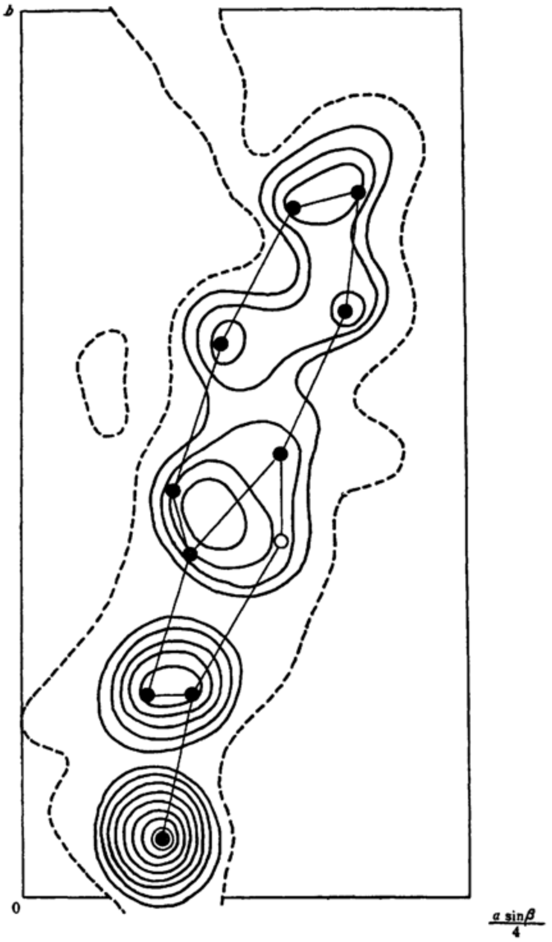

Fig. 4. The final Fourier projection of the electron density along the c axis. Contours at intervals of 2 eÅ^{-2}. Contour at 2 Å^{-2} is broken.

Cl–Cl vector. Therefore, the trial method was applied to $(h\,0\,l)$ first, in order to obtain the x and z coordinates of all atoms. After satisfactory x and z coordinates were determined, y coordinates were estimated by the trial for $(h\,k\,0)$. Refinements of these atomic coordinates were made by successive two-dimensional Fourier and the least square method. The final atomic coordinates of the chlorine, nitrogen and carbon are listed in Table I. Calculated structure factors $F(h\,0\,l)$ and $F(h\,k\,0)$ are shown with broken lines in comparison with observed values (full lines) in Figs. 1 and 2 respectively. In the structure-factor calculations the atomic scattering factors were taken from McWeeny's paper[8], the values for "valence states" being used for carbon. The best B factors were 3.5 and 4.5 Å^2 for $(h\,0\,l)$ and $(h\,k\,0)$

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[8] R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

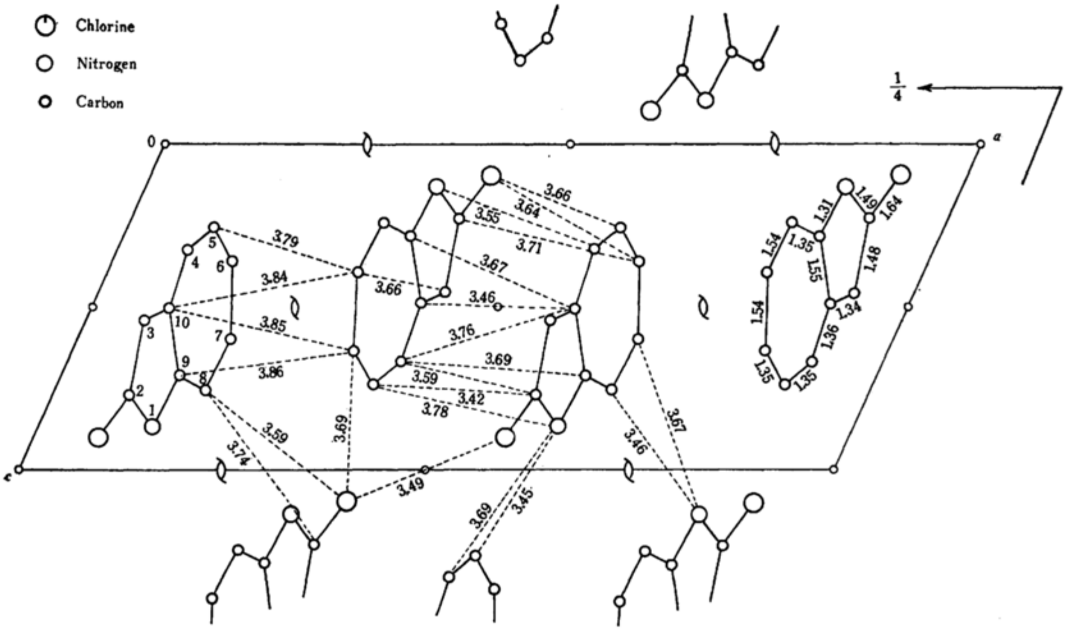

Fig. 5. Arrangement of molecules in the (010) projection, with intra- and intermolecular distances (Å).

respectively. At this stage, R indices become 0.176 for $(h\,0\,l)$ and 0.231 for $(h\,k\,0)$, if non-observed reflexions are omitted. The electron density projections along the b and c axes are shown in Figs. 3 and 4 respectively.

Description of the Structure.—As the scattering factors modified by thermal coefficients for nitrogen and carbon are hardly different, it is difficult at the earlier stage of analysis to decide which of the atoms, 1 or 3 numbered as shown in Fig. 5 corresponds to the nitrogen. If the atom at 3-position is nitrogen, the R index for $(h\,0\,l)$ becomes 0.185. On the other hand, if the atom at 1-position is nitrogen, the R index is 0.176 as described in the preceding paragraph. Moreover, the intermolecular distances show that the atom at 1-position has the near approaches to neighboring molecules such as 3.45 and 3.46 Å, which seem unreasonable for the CH–CH contacts. Thus it may be concluded that the atom at the 1-position is nitrogen.

Molecular dimensions (shown in Fig. 5) can not be discussed in detail in view of the rather large standard deviations of the coordinates.

Crystal structure projected along the b axis is shown in Fig. 5. There are no large discrepancies from the ordinarily accepted range of values for the intermolecular approaches. The long and short axes of the molecule make angles of about 50° and 30° with the (010) plane respectively. An outline of the molecular arrangement in this crystal seems to be of the intermediate type between those in azulene[9] and 1-oxa-azulan-2-one[4,5].

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[9] J. M. Robertson, H. M. M. Shearer, G. A. Sim and D. G. Watson, *Nature*, 182, 177 (1958).