Crystal Structures of Two Isomers of Bromo-methoxy Tropone

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Hitherto we have reported on the crystal structures of several compounds with a seven-membered carbon ring[1-9] in order to elucidate the structures of molecules, accurate molecular dimensions, and the types of molecular packing as a measure of the forces exerted between molecules. As a part of this series, this paper will deal with the crystal structures of two isomers of bromo-methoxy tropone. Remarkable differences in dipole moment and chemical behavior between these isomers have already been reported and discussed in relation to their conformations.[10,11] It is hoped that this paper's determination of their molecular structures will throw light on these problems.

Experimental

Crystals of two isomers of bromo-methoxy tropone, $C_8H_7O_2Br$, were kindly supplied by Professor Tetsuo Nozoe, Tohoku University. Both of these crystallize out in the form of needle-like prisms; the melting point is 91°C for the 7-bromo isomer (7-bromo-2-methoxy tropone) and 76°C for the 3-bromo isomer (3-bromo-2-methoxy tropone).

Oscillation and Weissenberg photographs were taken around two principal axes for each by means of the Cu$K\alpha$ radiation, and the multiple-film technique was used to correlate the strong and weak reflections. The intensities were estimated by visual comparison with a calibrated scale, and the corrections for polarization, Lorentz and absorption factors were made in the usual way.

The crystal data thus obtained, the dimensions of the crystals used, and the range of intensity observed are given below.

7-Bromo Isomer.—Four molecules in an orthorhombic unit cell with $a=26.56$, $b=6.09$, and $c=4.97$ Å. Absent spectra: $(hk0)$ when h is odd, $(0k0)$ when k is odd, and $(00l)$ when l is odd. Space group: $Pn2_1a$. Volume of the unit cell: 803.7 Å^3. Linear absorption coefficient for Cu$K\alpha$ radiation: $\mu=67.5\,\text{cm}^{-1}$. Total number of electrons per unit cell: $F(000)=424$. Rectangular dimensions of a cross section of crystals: 0.02×0.03 cm. for the c and b axis rotations. The relative intensities ranged from 1800 to 1 for $(hk0)$ reflections and from 1200 to 1 for $(h0l)$ reflections. Reflections from 92 planes were observed out of 108 possible $(hk0)$'s, and those from 129 planes out of 162 possible $(h0l)$'s.

3-Bromo Isomer.—Four molecules in a monoclinic unit cell with $a=7.64$, $b=26.57$, $c=3.99$ Å, and $\beta=101.5°$. Absent spectra: $(h0l)$ when h is odd, and $(0k0)$ when k is odd. Space group: $P2_1/a$. Volume of the unit cell: 793.7 Å.^{3} Linear absorption coefficient for CuK_α radiation: $\mu=68.2\,\text{cm}^{-1}$. Total number of electrons per unit cell: $F(000)=424$. Rectangular dimensions of a cross-section of crystals: 0.02×0.02 cm. and 0.03×0.04 cm. for the c and a axis rotations respectively. The relative intensities ranged from 510 to 1 for $(hk0)$ reflections and from 2210 to 1 for $(0kl)$ reflections. Reflections from 100 planes were observed out of 167 possible $(hk0)$'s, and those from 100 planes out of 121 possible $(h0l)$'s.

Structure Determination

7-Bromo Isomer.—A modified Patterson projection $P(UV)$ was synthesized, the modification factors being of the form of $(1/f)\cdot \exp B'(\sin\theta/\lambda)^2$, where f is the atomic scattering factor and an appropriate B' value is chosen to get a good resolution. This Patterson map showed not only the position of the bromine atom, but also clearly showed the shape of the molecule projected on the (001) plane, with an ambiguity for the methyl group. Two peaks were observed, both of which could be assigned to the methyl group. Thus, two sets of initial atomic coordinates were obtained, where the y coordinate of the bromine atom is taken arbitrarily to be zero because the b axis is polar in this space group. Atomic coordinates for each model structure

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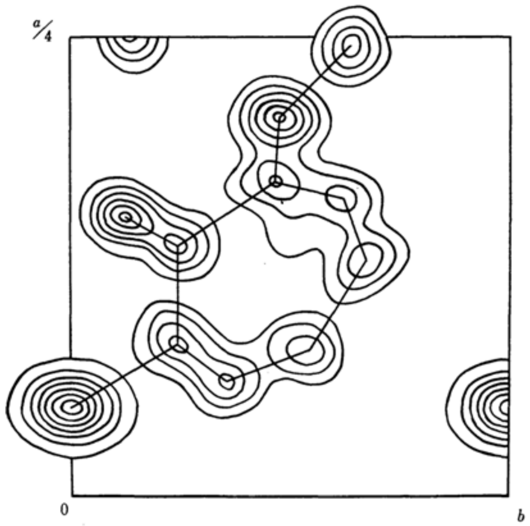
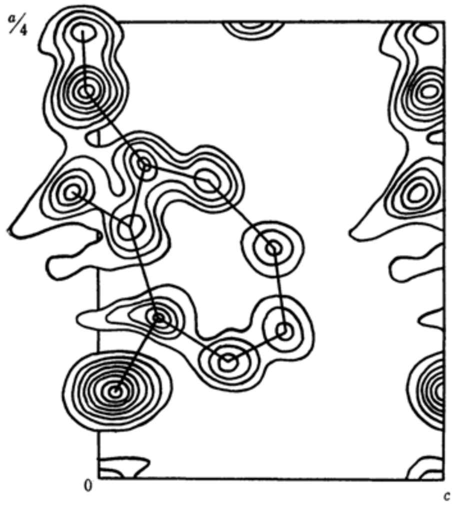
were refined by successive Fourier and partial difference syntheses. The rate of convergence was rather low because of the presence of the heavy atom and the lack of a center of symmetry. The Fourier projection derived from the first model structure contained, in addition to the peaks expected from the initial structure, an unnegligible peak at the position where the methyl group was assumed in the second model structure. Since successive Fourier refinements did not make this ghost peak disappear, the first model structure was abandoned. The second model structure gave a fairly reasonable electron density distribution and a better agreement between observed and calculated structure factors than did the first model. The final electron density projection on the (001) plane is shown in Fig. 1 (a). The discrepancy index, $\sum||F_o|-|F_c||/\sum|F_o|$, reduced to 0.150 for ($hk0$) reflections if non-observed reflections were omitted. The best over-all temperature factor, B, was 4.4 Å^2.



the c axis downward

Fig. 1 (a)



the b axis upward

Fig. 1 (b)

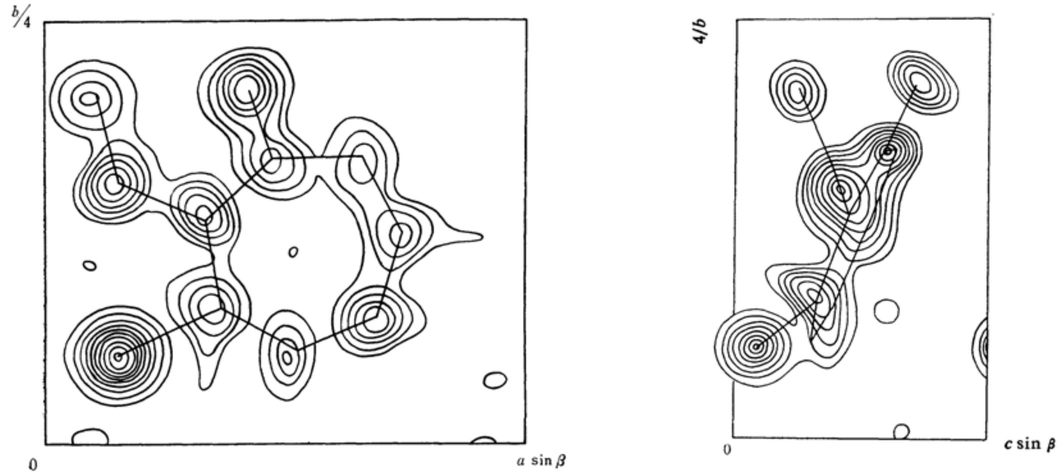
Fig. 1. Electron density of 7-bromo-2-methoxy tropone projected along (a) the c and (b) the b axes. Contours at equi-intervals in an arbitrary scale. One for every five countour lines are drawn around the bromine atom.

The coordinates of the bromine atom in the (010) projection were deduced easily from the Patterson function, $P(UW)$. The first Fourier projection of the electron density in this plane, calculated with $F(h0l)$'s of signs which result from the bromine atom alone, definitely showed the positions of all the atoms in the molecule. The atomic coordinates were refined by the successive Fourier method. The final electron density projection on the (010) plane is shown in Fig. 1(b); the discrepancy index was 0.181 for the ($h0l$) zone if non-observed reflections were omitted. The best over-all B factor was 3.0 Å^2.

Although a significant anisotropic thermal motion of the bromine atom was observed from the two projections of the electron density distribution, no correction was made for anisotropic temperature factors. The final atomic coordinates are listed in Table I(a),

TABLE I. ATOMIC COORDINATES

	Atom	x/a	y/b	z/c
(a)	7-Bromo-2-methoxy tropone			
	Br	0.047_6	0.000	0.047
	O_1	0.154	0.122	−0.069
	O_2	0.208	0.472	−0.031
	C_1	0.138	0.258	0.100
	C_2	0.170	0.450	0.133
	C_3	0.163	0.626	0.327
	C_4	0.126	0.675	0.515
	C_5	0.082	0.543	0.542
	C_6	0.065	0.357	0.393
	C_7	0.087	0.248	0.180
	CH_3	0.245	0.637	−0.037
(b)	3-Bromo-2-methoxy tropone			
	Br	0.149_9	0.054_2	0.092_9
	O_1	0.423	0.209	0.711
	O_2	0.154	0.157	0.390
	C_1	0.467	0.169	0.590
	C_2	0.330	0.133	0.450
	C_3	0.364	0.082	0.330
	C_4	0.525	0.056	0.300
	C_5	0.690	0.078	0.390
	C_6	0.738	0.126	0.530
	C_7	0.653	0.171	0.640
	CH_3	0.110	0.209	0.240



the c axis upward

Fig. 2(a)

the a axis downward

Fig. 2(b)

Fig. 2. Electron density of 3-bromo-2-methoxy tropone projected along (a) the c and (b) the a axes. Contours at equi-intervals on an arbitrary scale. One for every five contour lines are drawn around the bromine atom.

where the x coordinates are the weighted mean of those obtained from the two projections.

3-Bromo Isomer.—The first clue to an approximate structure was obtained, much as in the case of the 7-bromo isomer, by the modified Patterson function, $P(UV)$, along the short c axis. The refinement of each atomic coordinate thus obtained was also done by successive Fourier and partial difference syntheses.

With reference to the x and y coordinates of atoms, the z parameter of each atom was estimated by the trial-and-error method and was refined by the ordinary Fourier method. The final electron density projections along the c and a axes are shown in Figs. 2 (a) and (b) respectively. The final atomic coordinates are listed in Table I(b) ; the best over-all B factor was found to be 4.0 Å^2. At this stage, the discrepancy indices reduced to 0.152 for ($hk0$) and 0.172 for ($0kl$) if non-observed reflections were omitted.

Discussion

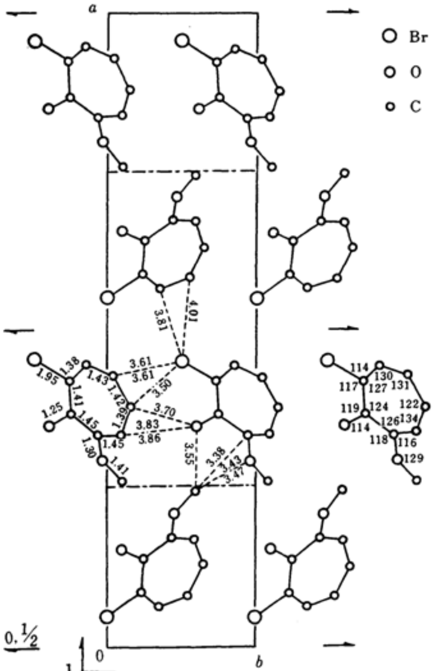
The position of the substituted bromine atom in each isomer was established without any ambiguity from the Fourier projections of the electron density, thus confirming the structural formulae assigned to the two isomers by organo-chemical research.[11]

As a result of the disturbance of the heavy atom, the atomic coordinates are not very accurate, the accuracies of bond lengths being estimated to be about 0.1 Å or more. Within the limits of errors, all the bond lengths and angles shown in Figs. 3 (a) and (b) are considered to be normal. Although the seven-membered carbon ring is found to be approximately planar, the methoxy oxygen, the carbonyl oxygen and the bromine atoms deviate significantly from the ring plane, alternately in opposite directions, so as to keep away from each other.

Another point to be discussed is the conformation of the methoxy group. Let us call three typical conformations the perpendicular, cis and trans forms. In the perpendicular form the methyl group lies on a plane perpendicular to the ring through O_2 and C_2, while in the cis and trans forms the methyl group is located on the ring plane nearest to and furthest from the carbonyl oxygen atom respectively. The methoxy group of the 3-bromo isomer takes a conformation between the cis and perpendicular forms, while that of the 7-bromo isomer has a conformation between the perpendicular and trans forms. These conformations might be caused by a great steric repulsion from the bromine atom and are in agreement with the chemical fact that the 3-bromo isomer is more liable to aromatization than is the 7-bromo isomer.[11]

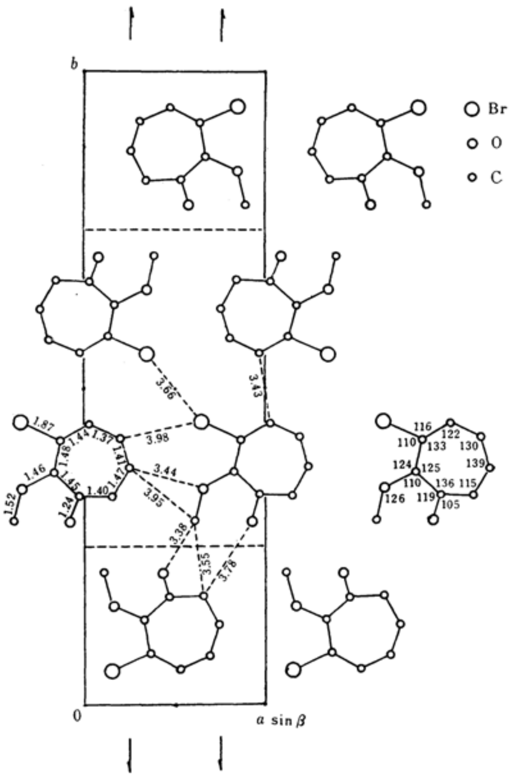
The dipole moments of these isomers have been measured and compared with the theoretical values for various conformations by Kurita, Seto, Nozoe and Kubo.[10] According to these authors, the observed moments of the 3-bromo and the 7-bromo isomers (3.31 D for the former and 5.51 D for the latter) are closest to the theoretical values for the cis and perpendicular form respectively. Although the structure of the molecule in crystalline states is not necessarily the same as that in solutions, the molecular structure of the two isomers described in this paper are compatible with the conclusion derived from the dipole moment measurements.

The crystal structure projected along the c axis of the 7-bromo isomer and that projected along the c axis of the 3-bromo isomer are shown in Figs. 3(a) and (b) respectively. It should be noted that the features of molecular arrangement in the crystals of the two isomers are very similar, as can be seen in the lower-half cells shown in Figs. 3(a) and (b), in spite of a considerable difference in the dipole moments of the two isomers. However, while the upper-half cell of the 3-bromo isomer is antiparallel to the lower with respect to the direction of the C–Br bond, so that the crystal is centro-symmetric, the upper-half cell of the 7-bromo isomer is parallel to the lower, so that the crystal is polar. The difference in the melting points of the two compounds is probably connected with this difference in their molecular arrangement.



the c axis downward

Fig. 3(a)



the c axis upward

Fig. 3(b)

Fig. 3. Crystal structure of (a) 7-bromo- and (b) 3-bromo-2-methoxy tropone, with interatomic distances (Å) and bond angles (°).

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