A Refinement of the Crystal Structure of Tropolone Hydrochloride

By Yoshio SASADA and Isamu NITTA

(Received September 27, 1956)

Introduction

Previously we have reported the crystal structure of tropolone hydrochloride as an example of successful application of the inequality method[1]. Owing to the following two reasons we had for a time to abandon further refinements of the structure: (i) The crystals are considerably hygroscopic and unstable. Even the specimens sealed in the borosilicate capillaries were decomposed in summertime, giving Debye-Scherrer patterns together with single crystal reflexions of this compound. (ii) Crystals with suitable form were rather few and much of them were twinned. Therefore it was impossible to obtain reliable data for the general (hkl) reflexions except for ($0kl$). Thus we had to be contented with the approximate crystal structure described in the previous paper.

On the other hand, we have investigated the crystal structure of sodium tropolonate by means of (F_o-F_c) and three-dimensional Fourier techniques and obtained very accurate molecular dimensions together with approximate positions of hydrogen atoms and some knowledge of anisotropic thermal vibrations[2].

As emphasized in the previous papers[1,2], the comparative determinations of accurate structures of tropolone, its anion and cation are very interesting problems of the structural chemistry of tropolone derivatives. Moreover it will be significant in the case of cation to determine, if possible, directly the positions of hydrogen atoms attached to oxygen, which were supposed to be somewhere between O and Cl atoms. Such situations made us hope to re-investigate the crystal structure of hydrochloride. Fortunately, at this time Nozoe and his collaborators brought us suitable specimens of this compound and we have been able to find non-twinned crystals among them. This account will describe the refinement of the structure based on new sets of three-dimensional data obtained from integrated Weissenberg photographs with multiple-film technique, the main features of the structure, of course, being unchanged.

Crystal Data and Intensity Measurement

Crystals were obtained from ethanol-ether solution saturated with hydrogen chloride gas as white needles[3], elongated in the a axis direction.

Crystallographic and physical data obtained are:

Tropolone hydrochloride $C_7H_7O_2Cl$: m. p. 125–130°C, monoclinic,

$$a=4.71\pm0.02\ \text{Å},\quad b=18.01\pm0.03\ \text{Å},$$
$$c=8.56\pm0.03\ \text{Å},\quad \beta=98.2^\circ\pm0.5^\circ.$$

Absent spectra: ($h0l$) when l is odd, ($0k0$) when k is odd. Space group $P2_1/c$. Four formula units per cell. Volume of unit cell=718 Å^3.

Density (by floatation)=1.43,

Density (calc.)=1.47 g.cm^{-3}.

Linear absorption coefficient for Cu K_α radiation, $\mu=42.0\ \text{cm}^{-1}$. Total number of electrons per unit cell, $F(000)=328$.

These cell dimensions slightly differ from those reported in the previous paper[1]. The differences are mainly due to low accuracy of previous value of β.

In order to refine the atomic coordinates and to reveal the positions of hydrogen atoms by (F_o-F_c) syntheses, it is necessary to use considerably accurate intensity data. Two complete sets of relative intensities for ($0kl$), ($1kl$), ($2kl$) and ($3kl$) were obtained by the integrated Weissenberg procedures. The specimens used have the following maximum and minimum dimensions at right angle to the axis of rotation:

Crystal 1: 0.04×0.02; Crystal 2: 0.03×0.02 cm.

Intensities were estimated by visual comparison with the calibrated scale. The multiple-film technique was used to correlate strong and weak reflexions, ranging in relative intensities from 6000 to 1 for ($0kl$) zone. The corrections for absorption were made in the usual way only for ($0kl$). The values of structure factors used in the following analysis are the weighted means of the values in the above-mentioned two sets. Reflexions from 150 planes were observed out of 186 possible ($0kl$)'s and 458 out of 995 (hkl)'s.

Refinement of Atomic Coordinates and Location of the Hydrogen Atoms.

Starting from the approximate structure

---

[1] Y. Sasada, K. Osaki and I. Nitta, *Acta Cryst.* **7**, 113, (1954).

[2] Y. Sasada and I. Nitta, ibid., **9**, 205 (1956).

[3] T. Nozoe, S. Seto, T. Mukai. K. Yamane and A. Matsukuma, *Proc. Japan Acad.*, **27**, 224 (1951).

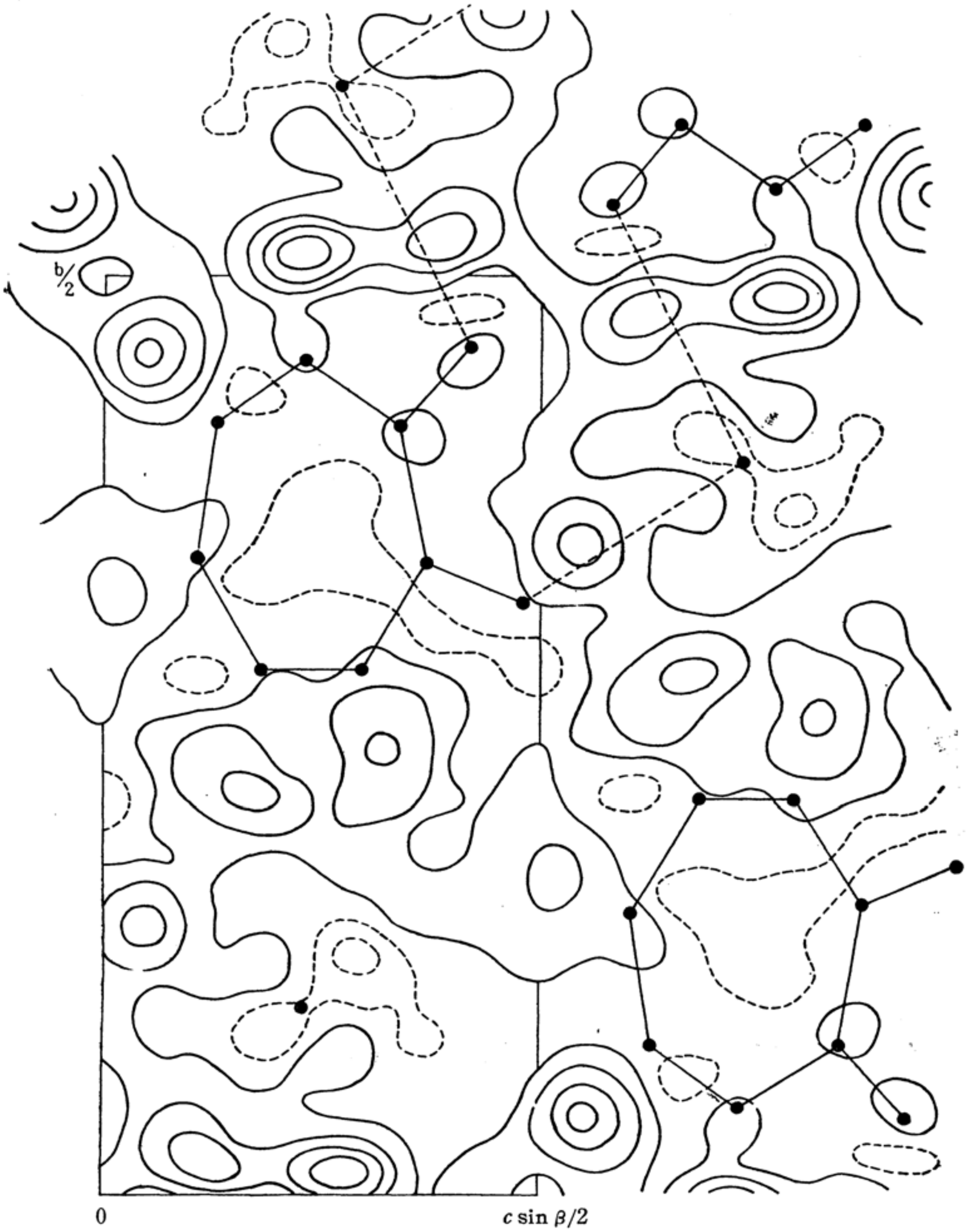

Fig. 1. The final $(Fo-Fc)$ projection along the a axis. Contours at intervals of $0.2\,\mathrm{e\AA^{-2}}$ with the lowest solid contour at $0.2\,\mathrm{e\AA^{-2}}$.

projected along the a axis mentioned in the previous paper[1], (at this stage the value of $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0.168, unobserved reflexions being omitted), successive refinements by (F_o-F_c) syntheses were made[4]. In the structure-factor calculation, the atomic scattering factors were taken from McWeeny[5], using for oxygen $\bar{f}_0=\frac{1}{3}(f^{\parallel}+2f^{\perp})$, and for carbon the values for 'valence states'.

It was observed from the $(\rho_o-\rho_c)$ maps that the thermal vibration of chlorine ion was considerably anisotropic. Consequently scattering factor of form, $f=f_0\exp[-\{\alpha+\beta\sin^2(\varphi-\psi_c)\}(\sin\theta/\lambda)^2]$ were employed[4,6] for this atom, where α and β

---

4) W. Cochran, *Acta Cryst.*, **4**, 81 (1951).

5) R. McWeeny, ibid., **4**, 513 (1951).

6) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

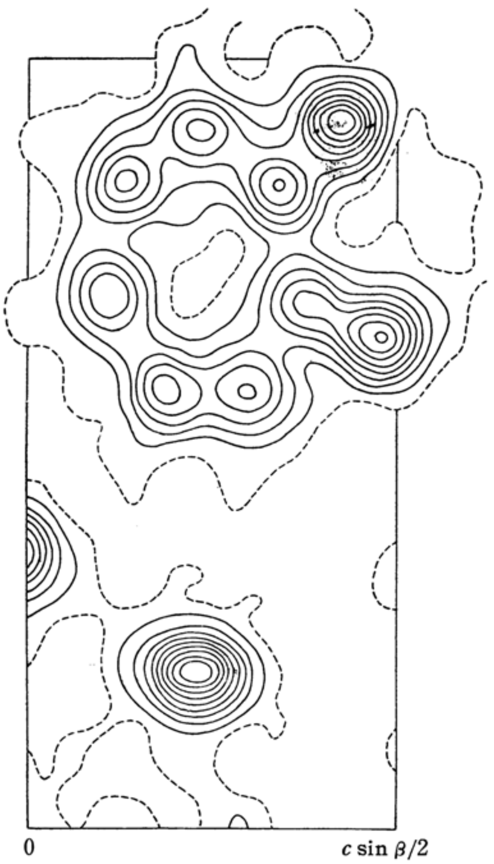

Fig. 2. The final Fourier projection of the electron density along the a axis. Contours at intervals of 2Å^{-2} for chlorine and those at intervals of $1\,e\text{Å}^{-2}$ for the other atoms. Contour at $1\,e\text{Å}^{-2}$ is broken.

are constants, ψ_c is the angle between the direction of maximum vibration and the c axis, and $(2\sin\theta,\ \varphi)$ are the polar coordinates of a point in the $(0kl)$ section of the reciprocal lattice, measured from the b^* axis. In the projection it should be noted that only two chlorine ions are equivalent in relation to anisotropic vibrations. As thermal motions of the other atoms were not significantly anisotropic, ordinary B factors were applied. The assignments of these thermal constants proceeded simultaneously with the refinement of atomic coordinates. (The detailed procedures will be shown elswhere⁷⁾.) The best thermal factors deduced from the seventh $(\rho_o-\rho_c)$ map were:

$B=5.55$ for oxygen, 5.15 for C_1 and C_2, 5.95 for $C_3 \cdots\cdots C_7$, 5.75 for H and $\{3.75+4.0\sin^2(\varphi-25°)\}$ for chlorine.

The R index for $(0kl)$ was 0.071 including the contributions from hydrogen atoms.

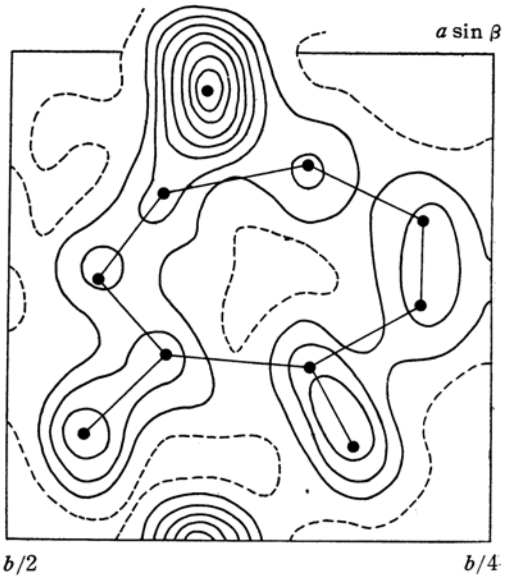

Fig. 3. The final Fourier projection of the electron density along the c axis. Contours at intervals of $2\,e\text{Å}^{-2}$, that at $2\,e\text{Å}^{-2}$ being broken. Black circles show the final atomic positions.

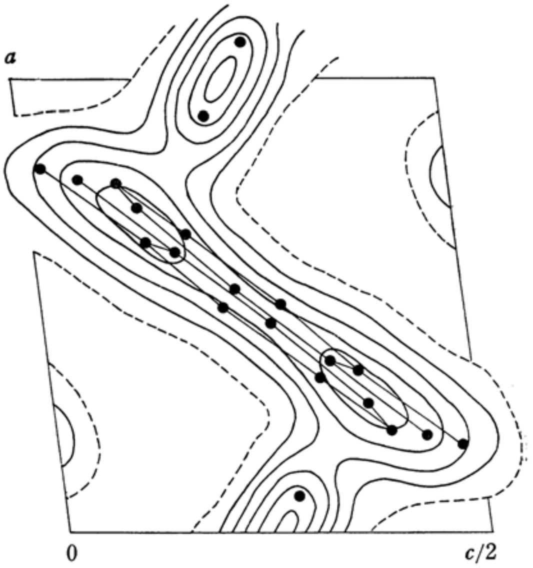

Fig. 4. The final Fourier projection of the electron density along the b axis. Contours at intervals of $4\,e\text{Å}^{-2}$, that at $4\,e\text{Å}^{-2}$ being broken. Black circles show the final atomic positions.

The final $(\rho_o-\rho_c)$ map (the eighth) is shown in Fig. 1. The significant peaks are evidently due to the hydrogen atoms. It should be emphasized that the positions of some hydrogen atoms, especially one attached to O_2, are revealed after the full correction was made for anisotropic motion of chlorine.

---

7) Y. Sasada and I. Nitta, Unpublished.

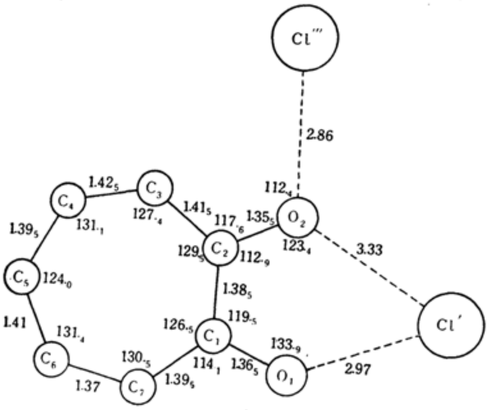

Fig. 5. Bond lengths (Å) and bond angles (°).

As the projections along the b and c axes were unsuitable for refinement owing to considerable overlapping, the x-coordinates of the carbon, oxygen and chlorine atoms were determined by successive three-dimensional line syntheses through atomic centres. Series termination errors were corrected by means of the back-shifts[8]. In the structure-factor calculation for (hkl), the mean value of B, 4.8, was used and the contributions from the hydrogen atoms were omitted. That the B for (hkl) came out smaller than those for ($0kl$) was mainly due to the omission of correction for absorption. The R index was 0.227 for (hkl), (0.127 unobserved reflexions being omitted).

The final electron density projections along three principal axes are shown in Figs. 2, 3 and 4.

Coordinates, Molecular Dimensions and Estimation of Accuracy

The final values of the coordinates of carbon, oxygen and chlorine atoms are shown in Table I. The coordinates x, y and z are referred to the monoclinic axes, and X', Y and Z' referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes.

TABLE I

ATOMIC COORDINATES

Atom	y/b	z/c	x/a	Y(Å)	Z'(Å)	X'(Å)
Cl	0.1015	0.2268	−0.075	1.828	1.921	−0.630
O_1	0.3205	0.4785	0.191	5.772	4.053	0.316
O_2	0.4610	0.4200	0.217	8.303	3.557	0.509
C_1	0.3430	0.3680	0.355	6.177	3.117	1.223
C_2	0.4180	0.3350	0.375	7.528	2.837	1.357
C_3	0.4540	0.2280	0.533	8.177	1.931	2.232
C_4	0.4200	0.1280	0.713	7.564	1.084	3.202
C_5	0.3455	0.1030	0.773	6.222	0.872	3.515
C_6	0.2860	0.1795	0.655	5.151	1.520	2.866
C_7	0.2850	0.2960	0.483	5.133	2.507	1.914

The bond lengths and valency angles in the tropolone ring are shown in Fig. 5.

The standard deviations of the atomic coordinates, $\sigma(x)$, etc., were estimated using

$$\sigma(x)=\frac{1}{V}\frac{2\pi}{a}\{\sum h^2\sigma^2(F)\}^{\frac{1}{2}}\Big/\left|\frac{\partial^2\rho_3}{\partial x^2}\right|,$$

$$\sigma(y)=\frac{1}{A}\frac{2\pi}{b}\{\sum k^2\sigma^2(F)\}^{\frac{1}{2}}\Big/\left|\frac{\partial^2\rho_2}{\partial y^2}\right|$$

and the corresponding expression for $\sigma(z)$[9,10], where A is the area of the cell projection, V the volume of the cell, $\sigma(F)$ the standard deviation of F values, $\frac{\partial^2\rho_3}{\partial x^2}$ the curvature of the three-dimensional electronic density at the atomic centre, and $\frac{\partial^2\rho_2}{\partial y^2}$ the curvature of two-dimensional density. In evaluating these expressions, we have taken $\sigma(F)=||F_o|-|F_c||$. The curvature was estimated by assuming that the electron density within 0.4 Å from the atomic centre can be represented by the Gaussian distribution, so that $\partial^2\rho/\partial x^2=-2p\rho(0)$. The constant p was evaluated by graphical plots of $\log\rho$ against r^2 from the final F_0 synthesis.

The coordinate standard deviations obtained by these methods were:

$\sigma(y)=\sigma(z)=0.003$, $\sigma(x)=0.004$ Å for chlorine,
$\sigma(y)=\sigma(z)=0.008$, $\sigma(x)=0.010$ Å for oxygen,
$\sigma(y)=\sigma(z)=0.015$, $\sigma(x)=0.017$ Å for carbon.

From these results the standard deviation of a C–C bond comes out to be about 0.023 Å and that of a C–O bond about 0.018 Å. The average standard deviation of bond angles computed by the equation given by Ahmed and Cruickshank[11] was found to be 1.4°. The standard deviation of electron density, given by

$$\sigma(\rho)=\frac{1}{A}\{\sum(|F_o|-|F_c|)^2\}^{\frac{1}{2}},$$

was found to be 0.17 eÅ^{-2} for the projection along the a axis.

Discussion

Planarity of Tropolone Ring.—First it

---

[8] A. D. Booth, *Proc. Roy. Soc.*, (London), **A188**, 77 (1946).

[9] D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

[10] D. W. J. Cruickshank, ibid., **7**. 519 (1954).

[11] F. R. Ahmed and D. W. J. Cruickshank, ibid., **6**, 385 (1953).

will be examined more in detail whether all atoms in tropolone ring lie on one plane or not. By least squares the best plane through seven carbon atoms was determined to be

$$X' = -0.0786\,Y - 1.0257\,Z' + 4.8786. \quad (1)$$

The perpendicular displacements of the carbon atoms from this plane are listed in Table II. From the standard deviations of atomic coordinates only the displacement of C_6 is possibly significant. However, it will be noticed that there is a systematic variation in the displacements. In order to confirm this the χ^2 test was applied[12]. The value of χ^2 is 8.92 and $n=4$, then $P=0.06$; that is seven-membered carbon ring is not truly planar.

If O_1 and O_2 were included in the calculation, the mean plane was

$$X' = -0.0907\,Y - 1.0246\,Z' + 4.9546, \quad (2)$$

and perpendicular displacements are also listed in Table II. In this case, the displacements of O_1, O_2, C_4 and C_6 seem to be possibly significant. But χ^2 test shows that $P=0.0001$; that is, the deviation from this plane is highly significant.

TABLE II

PERPENDICULAR DISPLACEMENTS OF ATOMS FROM POSSIBLE MOLECULAR PLANES (Å)

Atom	Plane (1)	Plane (2)
O_1	$+0.03_2$	$+0.02_6$
O_2	-0.04_8	-0.03_3
C_1	$+0.01_7$	$+0.01_7$
C_2	-0.01_4	-0.00_5
C_3	-0.01_7	-0.00_1
C_4	$+0.02_1$	$+0.03_1$
C_5	$+0.01_3$	$+0.01_3$
C_6	-0.03_4	-0.04_4
C_7	$+0.00_6$	-0.00_5
Cl′	$+0.52_9$	
Cl″	-1.13_9	
O_2'	-0.56_2	

Thus we may say only that the tropolone ring deviates slightly from a strictly planar form. It seems to be likely from the molecular packing and somewhat shorter intermolecular distances between particular atoms that such deviations may be due to some effects of crystalline field or others.

Intramolecular Distances.—The C–O distances are 1.355 and 1.365 Å as shown in Fig. 5. From the significant test, the two C–O bonds are of the same nature. The identical character of the two C–O bonds, which have been observed in the case of sodium tropolonate[2] (mean C–O length; 1.285 Å), is an essentially different feature from the case of neutral tropolone, in which C–O lengths are 1.26 and 1.34 Å[13]. As previously mentioned, these three compounds are isoelectronic with respect to the π-electron system. It is noted that the mean values of two C–O distances become larger when the number of added protons increases.

The mean C–O length, 1.360 Å in the present case, is in good agreement with those in the structures of resorcinol[14,15] and 1–4 dimethoxy benzene[16].

The canonical formulae of the Kekulé type with formal charges are shown in Fig. 6. In terms of the resonance theory, the bond lengths observed will imply that, in the actual ground state, the contributions from the structures of the type (B), including III–IX, should be considered to be more appreciable than those of the type (A). It agreed with the famous conclusion[17] that the seven-membered carbon ring prefers to lose one electron to form the stable 6π electron system, and with also more recent molecular orbital calculation of tropolone[18]. It can further account for the measurement of dipole moment[19] and some chemical evidences[20].

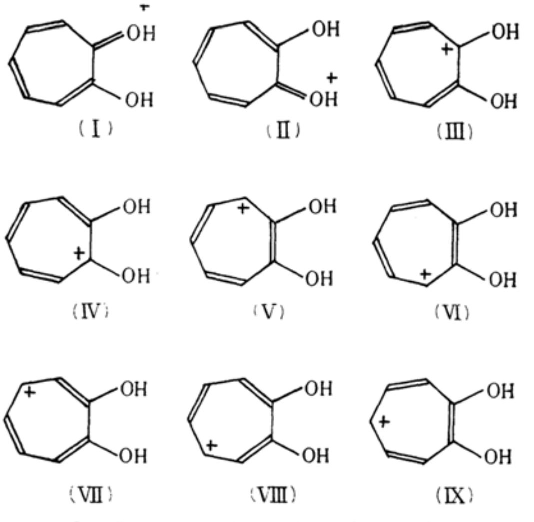

Fig. 6. Canonical formulae of tropolonium cation.

---

[12] P. J. Wheatley, *Acta Cryst.*, **6**, 369 (1953).

[13] M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).

[14] J. M. Robertson, *Proc. Roy. Soc.* (*London*)., **A 157**, 79 (1936).

[15] J. M. Robertson, ibid., **A167**, 122 (1938).

[16] T. H. Goodwin, M. Przybylska and J. M. Robertson. *Acta Cryst.*, **3**, 279 (1950).

[17] E. Hückel, *Z. Physik*, **70**, 204 (1931).

[18] Y. Kurita and M. Kubo, This Bulletin, **24**, 13 (1951).

[19] Y. Kurita, T. Nozoe and M. Kubo, ibid., **24**, 10 (1951).

[20] T. Nozoe, *Proc. Japan Acad.*, **26**, 30 (1950).

As the standard deviations of the C–C bonds are about 0.023 Å, the bond C_6–C_7 is shorter than the bonds C_2–C_3 and C_3–C_4 significantly, while the other fluctuations among the bonds can not be discussed seriously. The significant fluctuations among the seven C–C bonds show evidently that the contributions from the component structures of the type B are not equal. As complete interpretation of this fact is not yet given, we will only present some qualitative considerations. The first reason will be the non-equivalent orientations of the two O–H bonds with respect to the line through C_5 and the mid-point of C_1–C_2. In 1–4 dimethoxy benzene[16] the C–C bond in the cis-position to the methyl group is greater than that in the trans-position significantly (1.44 and 1.36 Å). The same situation is observed in the molecule of hydroquinone in the quinhydron crystal (1.42 and 1.34 Å[21]). However, it is not the case for the structure of resorcinol, although the accuracy of the analysis is rather low[14,15]. For a quantitative discussion, it will be desirable to make complete structure analysis of catechol[22,23].

The second reason is the rather closer approaches of chlorine ions to some ring atoms; that is, C_3, C_5 and C_6 as shown in Fig. 8. These values are smaller than those in similar cases, that is, 3.85 Å in aniline hydrochloride[24], 3.63 Å in *m*-toluidine dihydrochloride[25], 3.71 Å in adenine hydrochloride[4], 3.56 Å in guanine hydrochloride[26]. At twin boundary in the crystal of *m*-toluidine dihydrochloride[25] the nearest approaches between carbon and chlorine are 3.52 Å, but this value seems to be less significant. It will be natural to consider that these carbon atoms close to chlorine ions become more positively charged than the others. If we use the terms of the resonance theory, it corresponds to the increased contributions of the components, V, VIII and IX.

The best agreement between measured and calculated bond lengths was obtained taking the following contributions:

I–II, each 11%, III and VII–IX, each 10%, IV and VI, each 4%, V, 30%, the relation $R=R_1-(R_1-R_2)3x/(2x+1)$[27], where x is double bond character, being used with $R_1=1.54$ (C–C), $R_2=1.34$ (C=C), $R_1=1.42$ (C–O) and $R_2=1.20$ Å (C=O). The calculated values are shown in Fig. 7(b), together with observed values in the present crystal (a) and in sodium tropolonate(c).

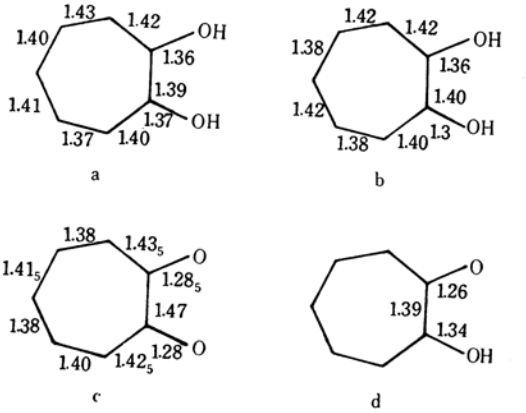

Fig. 7. (a) Observed bond lengths.
(b) Bond lengths calculated, using Pauling's relation.
(c) Bond lengths in tropolonate anion.
(d) Bond lengths in neutral tropolone.

Hydrogen Bonding and Molecular Arrangement.—The refined values for O···Cl are 2.97 and 2.86 Å, and are slightly shorter than those in chloral hydrate[28] (3.05kX),

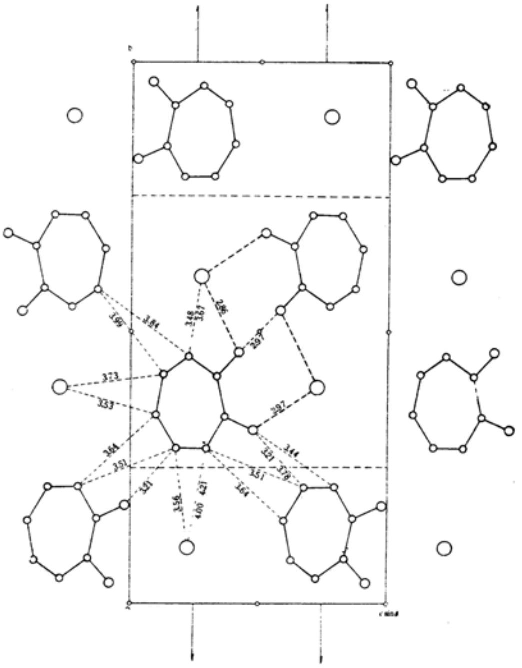

Fig. 8. Arrangement of molecules projected along the *a* axis.

---

[21] I. Nitta, K. Osaki and H. Matsuda, To be published.

[22] W. A. Caspari, *J. Chem. Soc.*, **1926**, 573.

[23] A. N. Sarker, *Phil. Mag.*, **2**. 1153 (1926).

[24] C. J. Brown, *Acta Cryst.*, **2**,228 (1949).

[25] F. Fowweather and A. Hargreaves, ibid., **3**, 81 (1950).

[26] J. M. Broomhead, ibid., **4**, 92 (1951).

[27] L. Pauling, "The nature of the chemical bond" (1948).

[28] S. Kondo and I. Nitta, *X-ray*, **6**, 53, (1950).

hydroxyl ammonium chloride[29] (2.99 Å), guanine hydrochloride[26] (3.16 Å), adenine hydrochloride[4] (C–H=0.95 and H···Cl=2.17 Å), ephedrine hydrochloride[30] (3.06 Å) and D(–) isoleucine hydrochloride[31] (3.05, 3.07 and 3.24 Å). Although it seems to be not quite reasonable to claim the hydrogen bonding only from these distances, the angles C–O–Cl, 133.9° and 112.4°, are favourable to hydrogen bond formation. Further this conclusion is supported evidently by the direct determination of the positions of hydrogen atoms, as seen in Fig. 1. If the hydrogen bonds are operative in this crystal, the dimer formation linked by them may be concluded and it seems interesting in respect to the relation with the cystal structure of neutral tropolone, in which the presence of dimer was supposed[32]. Moreover, it is observed from the difference map that the anisotropic thermal motions of each atom seem to originate from the oscillation of the dimer, as a whole, about its centre.

Finally will be described an outline of the crystal structure ignoring, for the present, the dimer formation. Each tropolone ring was surrounded by six chlorine ions and each chlorine ion has six tropolone rings as first neighbours. The packing is closely related to ionic crystals of the NaCl type. This arrangement of chlorine ions and centres of gravities of tropolone rings also supports the above argument that the net positive charges distribute over the whole ring of the latter.

The authors wish to express their thanks to Professor T. Nozoe and his collaborators for supplying the specimens and also for continued encouragement. We are also indebted to the members of the group who have been making the cooperative physico-chemical investigations of "tropolone chemistry" for their helpful discussions. This research was supported by a grant from the Ministry of Education.

Department of Chemistry
Osaka University, Osaka

---

[29] B. Jerslev, *Acta Cryst.* **1**, 21, (1948).
[30] D. C. Phillips, ibid., **7**, 159, (1954).
[31] J. Trommel and J. M. Bijvoet, ibid., **7**, 703, (1954).
[32] K. Osaki and I. Nitta, Unpublished.