The Crystal Structure of Tropolone Hydrochloride

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Tropolone hydrochloride, $C_7H_5O(OH) . HCl$, is monoclinic with $a = 4.72 \pm 0.02$, $b = 18.01 \pm 0.03$, $c = 8.58 \pm 0.03$ Å, $\beta = 97° 50' \pm 30'$. The space group is $P2_1/c$ with four formula units per unit cell. By means of the Sakurai inequality chart, the projected electron density along the a axis was directly synthesized without any trial. It reveals the planar heptagon of carbon atoms, the mean C–C bond distance of which comes out to be 1.40 Å. The results of the analysis show the packing of $[C_7H_5(OH)_2]^+$ and Cl^- ions somewhat like that of ions in NaCl-type crystals.

Tropolone, $C_7H_5O(OH)$, is a compound of an interesting amphoteric nature; it forms crystalline salts not only with NaOH, but also with HCl. It is thus of significance to determine the structure of these salts in which tropolone behaves as anion in one case and as cation in the other. The present account contains an example of the direct determination of the structure of the hydrochloride by means of the inequality method, although previous electron diffraction (Heilbronner & Hedberg, 1951; Kimura & Kubo, 1953) and X-ray diffraction studies (Robertson, 1951; Nitta, Osaki & Ogawa, 1951; Dunitz, 1952; Taylor, 1952) have revealed the tropolone ring to be a planar heptagon.

The substance, $C_7H_5O(OH).HCl$, deposited in white needles from a solution of tropolone in CCl_4 by passing dry HCl gas, was recrystallized at room temperature from its ethanol–ether solution saturated with HCl gas, m.p. 125–130° C. (Nozoe *et al.*, 1951). As this substance is very hygroscopic and unstable, the sample was sealed in a thin-walled borosilicate capillary, and oscillation and Sauter photographs about the needle axis (a-axis) were taken, using Cu $K\alpha$ radiation. The dimensions of the unit cell, containing four formula units and of the space group symmetry $P2_1/c$, are

$$a = 4.72 \pm 0.02, \quad b = 18.01 \pm 0.03, \quad c = 8.58 \pm 0.03 \text{ Å},$$
$$\beta = 97° 50' \pm 30'.$$

Intensities were estimated visually, using a calibrated scale, by the multiple-film technique. The corrections for polarization and Lorentz factors were made in the usual way and that for absorption was neglected. Though only oscillation photographs about the one axis could be taken, owing to very small quantity of the sample and other experimental difficulties, it was to be expected from the short period of the a axis that the approximate molecular shape might be obtained from the electron-density projection along the a axis. In order to obtain this projection, the Harker–Kasper inequality (1948) was applied, using Sakurai's chart (1952) to determine the signs of the structure factors.

Unitary structure factors were deduced from the relative values of $F(0kl)$ as follows:

$$U(0kl) = KF(0kl) \exp B (\sin \theta / \lambda)^2 / f_C ,$$

where f_C is the scattering factor of carbon. The value of B was assumed to be 2.00 Å², and the scale factor K was chosen so that the average value of $U^2(0kl)$ was equal to

$$\Sigma z_i^2 / (\Sigma z_i)^2 = 0.0297 ,$$

where z_i is the number of electrons in the ith atom and the summation is taken over all atoms in the unit cell. The assumed value of B introduced a few contradictions among the signs thus obtained, so it was necessary to alter the value of B, or more conveniently the scale factor, by trial. After this the signs of 46 out of 83 reflexions with U larger than 0.04 were determined. The results of sign determination are given in Table 2, and in these signs two arbitrary parameters, ξ and η, should be included (Okaya & Nitta, 1952). The smallest unitary structure factor of which the sign could be determined was $U_{042} = 0.14$. None of the signs so determined was found to be incorrect after the final structure was established, thus justifying the above-mentioned correction. The electron density projected along the a axis was computed using these structure factors. As shown in Fig. 1, the approximate crystal structure with a seven-membered carbon ring was obtained without any ambiguity. Refinements of the parameters estimated from this projection were made by successive Fourier syntheses and by the trial-and-error method, and the final parameters are listed in Table 1, the comparison of calculated and observed structure factors being

Table 1. *Atomic parameters*

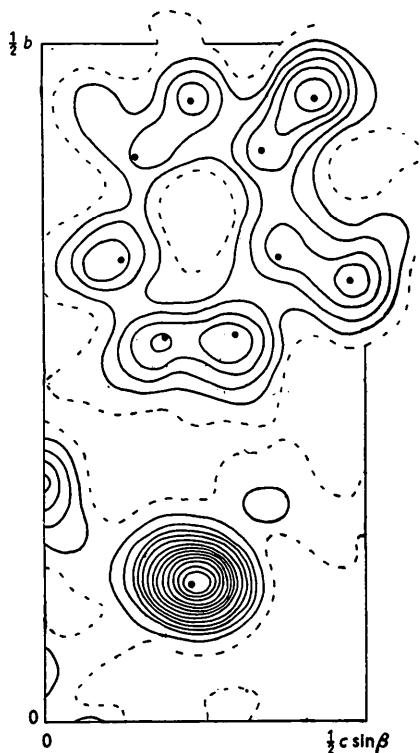| Atom	y/b	z/c	x/a
Cl	0.102	0.226	−0.075
O_1	0.325	0.475	0.180
O_2	0.458	0.422	0.210
C_1	0.344	0.365	0.360
C_2	0.421	0.339	0.409
C_3	0.458	0.228	0.566
C_4	0.417	0.142	0.753
C_5	0.342	0.120	0.799
C_6	0.285	0.187	0.678
C_7	0.287	0.298	0.485

Fig. 1. Electron-density projection along the a axis calculated using $F(0kl)$'s whose signs were determined by the inequality method. The black circles show the final atomic positions. Scale: 1 cm. = 1 Å.
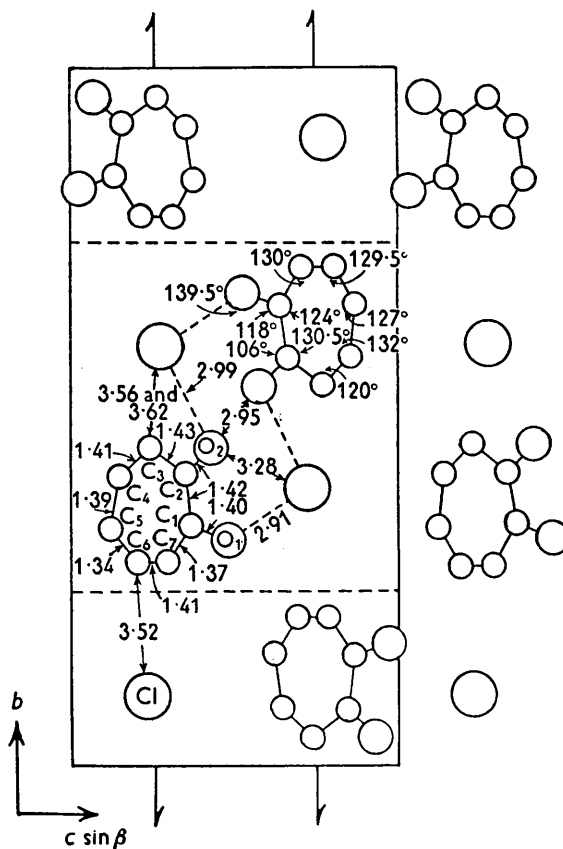

Fig. 2. Crystal structure of tropolone hydrochloride projected along the a axis. The main interatomic distances and bond angles are shown. Scale: 1 cm. = 2 Å.

given in Table 2. The reliability factor $R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$ amounts to 0·168 for the $(0kl)$ reflexions using the data up to $\sin\theta/\lambda = 0·620$, unobserved reflexions being omitted. In the structure-factor calculation, atomic scattering factors in the *International Tables* (1938) were used and the contributions from the hydrogen atoms were neglected. The best value of B was found to be 6·5 Å².

The crystal we could use in this experiment was twinned with (001) as the twinning plane, and there arose ambiguity in indexing the $(2kl)$ reflexions. Hence only the $(1kl)$ and $(\bar{1}kl)$ reflexions were used to estimate the approximate x-parameters by trial-and-error. Following similar reasoning to that used by Robertson (1951) in the case of cupric tropolone, the planarity of the tropolone ring may be concluded. This circumstance greatly simplified the determination of the x parameters, of which the obtained values are included in Table 1. The calculated and observed structure factors for the $(1kl)$ reflexions are given in Table 3. For the $(1kl)$ reflexions the reliability factor up to $\sin\theta/\lambda = 0·370$ was $R = 0·245$. Although the accuracy of the x-parameter values may thus be not very high, they will nevertheless be sufficient to deduce approximate interatomic distances because of the very short period of the a axis.

Calculated bond lengths and bond angles, using these parameters, are shown in Fig. 2. Although they

are not so accurate, it may be concluded that tropolone ring is an approximately planar heptagon in which the mean C–C distance is 1·40 Å. The C–O distances are 1·42 and 1·40 Å in this compound, while those in cupric tropolone are 1·25 and 1·34 Å (Robertson, 1951). These values clearly show the difference in the C–O bond nature between these two compounds. As shown in Fig. 2, each tropolone ring is surrounded by six chlorine atoms, and each chlorine atom has six rings as the nearest neighbours. The packing is closely related to ionic crystals of the NaCl type. The observed shortening of intermolecular C–Cl distances (Fig. 2), compared with those reported in similar cases such as aniline hydrochloride (Brown, 1949), m-tolidine dihydrochloride (Fowweather & Hargreaves, 1950) and adenine hydrochloride (Cochran, 1951), would mean a net positive charge distributed over the whole ring. These characteristics will support the following formula proposed by Nozoe (1951):
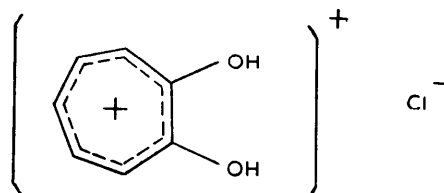
Table 2. *Calculated, observed and unitary structure factors and signs determined by the inequality method*

hkl	F_c	F_o	U	Sign
020	+2·9	2·9	0·08	—
040	-12·3	11·8	0·33	-1
060	-5·1	6·0	0·23	-1
080	-6·3	7·1	0·35	—
0,10,0	+3·2	2·7	0·17	—
0,12,0	+1·0	—	—	—
0,14,0	-2·6	2·7	0·22	-1
0,16,0	-4·0	3·6	0·36	-1
0,18,0	+1·2	1·2	—	—
0,20,0	+0·8	0·9	—	—
0,22,0	+0·1	—	—	—
011	+10·0	9·7	0·23	$\xi\eta$
031	+2·8	2·4	0·06	—
051	+3·2	4·1	0·14	—
071	-0·3	—	—	—
091	+3·6	2·8	0·15	—
0,11,1	+0·6	0·7	0·13	—
0,13,1	-1·7	2·5	0·18	$-\xi\eta$
0,15,1	-1·3	1·1	0·11	—
0,17,1	+0·5	—	—	—
0,19,1	+0·1	—	—	—
0,21,1	+0·1	—	—	—
002	-15·4	14·0	0·43	-1
022	-2·9	3·2	0·10	—
042	+5·3	3·6	0·14	+1
062	+12·3	14·7	0·56	+1
082	-3·6	4·2	0·23	-1
0,10,2	-6·2	7·1	0·47	-1
0,12,2	+1·2	—	—	—
0,14,2	+0·2	—	—	—
0,16,2	+2·2	2·5	0·25	+1
0,18,2	-0·6	0·9	—	—
0,20,2	-0·9	1·1	0·17	—
0,22,2	+0·1	—	—	—
013	-0·6	—	—	—
033	-1·3	0·7	0·04	—
053	+6·0	7·4	0·37	$\xi\eta$
073	+0·4	—	—	—
093	-3·5	3·6	0·25	$-\xi\eta$
0,11,3	-0·5	—	—	—
0,13,3	+0·1	—	—	—
0,15,3	+0·1	—	—	—
0,17,3	+0·5	—	—	—
0,19,3	-0·4	—	—	—
0,21,3	-0·1	—	—	—
004	+3·3	1·8	0·08	+1
024	+0·2	—	—	—
044	-1·6	0·9	—	—
064	-2·2	1·7	0·11	-1
084	+1·0	1·1	0·09	+1
0,10,4	+4·0	4·5	0·36	+1
0,12,4	-1·3	—	—	—
0,14,4	-2·7	2·4	0·25	-1
0,16,4	0·0	—	—	—
0,18,4	+0·8	—	—	—
0,20,4	+0·4	—	—	—
015	+2·1	2·1	0·14	—
035	-4·6	5·7	0·38	$-\xi\eta$
055	-3·0	3·5	0·25	—
075	-0·2	—	—	—
095	+1·9	1·8	0·15	—
0,11,5	+3·1	3·1	0·29	—
0,13,5	+0·4	—	—	—
0,15,5	-0·8	—	—	—
0,17,5	0·0	—	—	—
0,19,5	+0·3	—	—	—
006	-1·1	1·2	0·29	-1
026	-3·3	3·9	0·33	-1
046	+0·5	—	—	—
066	+1·0	—	—	—
086	-1·1	0·7	—	—
0,10,6	+0·1	—	—	—
0,12,6	+1·1	1·4	0·16	+1
0,14,6	+1·5	1·0	0·17	+1
0,16,6	+0·3	—	—	—
0,18,6	-0·3	—	—	—
017	-2·1	1·2	0·11	—
037	+0·1	—	—	—
057	+2·1	1·0	0·10	—
077	+1·0	1·0	—	—
097	-1·7	2·0	0·22	$-\xi\eta$
0,11,7	-0·6	—	—	—
0,13,7	+0·5	—	—	—
0,15,7	+0·6	—	—	—
008	+0·9	—	—	—
028	+0·3	—	—	—
048	-1·6	1·1	0·13	—
068	+0·3	—	—	—
088	+0·2	—	—	—
0,10,8	-0·1	—	—	—
0,12,8	+0·8	—	—	—
0,14,8	-0·3	—	—	—
019	+0·4	—	—	—
039	-0·6	—	—	—
059	-0·7	—	—	—
079	-0·2	—	—	—
099	+1·0	—	—	—
0,11,9	+0·4	—	—	—
0,0,10	-0·1	—	—	—
0,2,10	-0·4	—	—	—
0,4,10	+0·3	—	—	—
0,6,10	+0·2	—	—	—
021	+8·2	6·2	0·15	—
041	-5·8	5·0	0·15	$-\xi$
061	+15·7	18·3	0·61	ξ
081	+7·0	6·9	0·35	ξ
0,10,1	-0·9	0·9	0·06	—
0,12,1	-6·2	7·3	0·53	$-\xi$
0,14,1	-0·3	1·0	0·09	—
0,16,1	+1·9	1·7	0·17	ξ
0,18,1	0·0	—	—	—
0,20,1	-0·1	—	—	—
0,22,1	-0·9	1·5	0·25	$-\xi$
012	-0·3	—	—	—
032	-0·6	—	—	—
052	+2·0	1·4	0·06	—
072	+5·9	6·0	0·30	η
092	+2·1	2·2	0·14	—
0,11,2	-1·0	1·1	0·9	—
0,13,2	-1·0	—	—	—
0,15,2	-0·5	—	—	—
0,17,2	+0·4	—	—	—
0,19,2	0·0	1·3	0·17	—
0,21,2	-0·2	—	—	—
023	+14·0	14·8	0·55	ξ
043	+4·7	5·2	0·23	ξ
063	-4·5	4·9	0·25	$-\xi$
083	-0·5	1·0	0·07	—
0,10,3	-1·7	1·7	0·12	—
0,12,3	+3·1	3·9	0·33	ξ
0,14,3	+2·0	2·0	0·18	ξ
0,16,3	-1·6	1·0	0·22	$-\xi$
0,18,3	-1·0	1·0	0·12	—
0,20,3	0·0	—	—	—
014	+4·4	2·4	0·10	—
034	+5·1	3·9	0·22	η
054	+2·0	2·0	0·12	—
074	+0·6	—	—	—
094	0·0	—	—	—
0,11,4	+1·8	3·0	0·34	η
0,13,4	+1·3	1·0	—	—
0,15,4	-1·2	1·7	—	—
0,17,4	-1·3	1·3	0·15	—
0,19,4	-0·3	—	—	—
025	-5·0	5·0	0·35	$-\xi$
045	-1·8	1·1	0·09	$-\xi$
065	+4·2	4·8	0·36	ξ
085	+4·5	5·3	0·42	ξ
0,10,5	+0·9	1·4	0·12	—
0,12,5	-0·6	0·8	—	—
0,14,5	-1·8	1·5	0·22	—
0,16,5	-0·5	—	—	—
0,18,5	+0·5	—	—	—
016	-0·3	—	—	—
036	-2·8	2·3	0·22	$-\eta$
056	-0·6	—	—	—
076	+2·6	1·5	0·12	—
096	0·0	—	—	—
0,11,6	-1·3	—	—	—
0,13,6	-0·5	—	—	—
0,15,6	+0·3	—	—	—
0,17,6	+0·6	—	—	—
027	+1·7	1·2	0·15	—
047	-0·4	—	—	—
067	0·0	—	—	—
087	-2·2	2·1	0·22	$-\xi$
0,10,7	-0·1	—	—	—
0,12,7	+0·7	—	—	—
0,14,7	+0·2	—	—	—
0,16,7	0·0	—	—	—
018	+1·5	1·1	0·15	—
038	+1·7	1·4	0·13	—
058	-0·7	—	—	—
078	-0·7	—	—	—
098	-0·5	—	—	—
0,11,8	+0·1	—	—	—
0,13,8	+0·8	—	—	—
029	+0·3	—	—	—
049	-0·2	—	—	—
069	-0·4	—	—	—
089	+0·5	—	—	—
0,10,9	-0·7	—	—	—
0,1,10	-0·3	—	—	—
0,3,10	-0·9	—	—	—
0,5,10	-0·4	—	—	—
0,7,10	+0·4	—	—	—

The O–Cl distances are in good agreement with those found in the crystals of hydroxyammonium chloride (Jerslev, 1948) and chloral hydrate (Kondo & Nitta, 1950). The formation of dimer linked by these weak O · · · Cl hydrogen bonds may be concluded and it is interesting to compare this structure with that of tropolone (Osaki & Nitta, 1952), in which dimer formation was found. Further discussion will be given after the completion of the detailed analysis of the sodium salt now in progress.

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Table 3. *Calculated and observed structure factors for (1kl)*

hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
120	+ 3·7	3·6	173	−0·3	—	141	−3·5	2·5
140	−10·6	8·6	193	−5·5	3·6	161	−4·4	5·7
160	−2·3	1·3	1,11,3	−2·5	5·8	181	+2·7	2·1
180	+3·5	3·1	115	+5·1	2·8	1,10,1	+1·0	1·5
1,10,0	+4·3	3·8	135	−2·5	—	1,12,1	−1·9	—
1,12,0	+1·9	—	155	−2·7	—	123	+9·5	7·4
102	+18·5	22·7	1̄11	−3·1	3·0	143	+4·4	5·1
122	−1·5	—	1̄31	+0·4	—	163	+0·9	—
142	+5·1	5·3	1̄51	+5·3	3·8	183	−4·1	4·3
162	+5·0	3·4	1̄71	−1·2	—	1,10,3	+1·3	—
182	−7·3	7·6	1̄91	−0·7	—	125	+0·1	—
1,10,2	−5·5	5·3	1̄,11,1	−0·9	0·6	145	+0·6	—
1,12,2	−0·5	—	1̄13	−1·4	—	165	0	—
104	+3·7	3·8	1̄33	−5·7	5·6	1̄21	−3·0	2·2
124	+1·6	—	1̄53	−2·3	3·3	1̄41	−7·4	7·3
144	−3·1	3·3	1̄73	+0·4	—	1̄61	+5·5	4·7
164	+0·9	—	1̄93	+1·0	—	1̄81	+11·7	11·1
184	0	—	1̄,11,3	+2·7	1·2	1̄,10,1	−3·7	2·1
1,10,4	+0·4	—	1̄15	−0·4	—	1̄,12,1	−2·8	1·1
1̄02	−19·1	16·3	1̄35	−0·3	—	1̄23	+7·2	6·6
1̄22	−5·3	4·9	1̄55	−2·0	1·6	1̄43	+2·6	1·9
1̄42	+11·9	10·1	1̄75	+1·6	1·7	1̄63	−0·9	—
1̄62	+5·3	4·3	110	+2·1	0·9	1̄83	−2·3	2·1
1̄82	−1·8	—	130	+2·4	1·2	1̄,10,3	+1·1	2·0
1̄,10,2	−2·9	2·2	150	+0·4	—	1̄,12,3	+4·8	4·0
1̄,12,2	−2·5	1·2	170	−9·7	9·3	1̄25	−3·5	4·0
1̄04	+6·3	5·6	190	−2·8	1·7	1̄45	−5·1	5·8
1̄24	−1·1	1·6	1,11,0	+2·1	1·6	1̄65	+3·0	2·3
1̄44	−7·3	8·0	1,13,0	+0·3	1·2	1̄85	+1·1	—
1̄64	−5·3	6·0	112	−12·7	9·5	1̄12	+4·3	3·6
1̄84	+2·4	1·6	132	−7·5	3·4	1̄32	+1·2	—
1̄,10,4	+5·4	5·8	152	+0·8	—	1̄52	+3·0	2·3
111	+5·5	6·1	172	+1·0	2·5	1̄72	+4·4	4·4
131	+0·7	—	192	+2·7	1·5	1̄92	+0·4	—
151	−3·8	3·1	1,11,2	−1·0	—	1̄,11,2	+1·9	—
171	+0·7	—	114	+3·4	2·8	1̄14	+5·1	5·6
191	+0·6	—	134	+5·4	3·8	1̄34	+0·5	—
1,11,1	+1·8	4·5	154	+1·9	0·8	1̄54	−2·4	1·4
113	+1·3	—	174	−3·6	2·8	1̄74	−0·1	—
133	+0·4	—	194	−1·0	—	1̄94	−2·9	2·0
153	+7·9	6·2	121	−28·8	21·1	1̄16	0	—

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