Acta Cryst. (1956). **9**, 205

The Crystal and Molecular Structure of Sodium Tropolonate

By Yoshio Sasada and Isamu Nitta

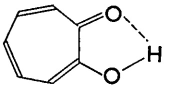
Faculty of Science, Osaka University, Nakanoshima, Osaka, Japan

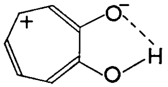
(*Received 5 August* 1955 *and in revised form* 12 *September* 1955)

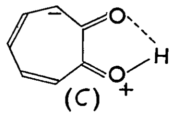
The crystal and molecular structure of sodium tropolonate (space group $P2_1/c$, $a = 13{\cdot}91$, $b = 3{\cdot}69$, $c = 11{\cdot}67$ Å, $\beta = 93{\cdot}1°$, 4 formula units per cell) has been accurately determined using two- and three-dimensional Fourier techniques and difference syntheses projected on the (010) plane. The final difference map reveals the hydrogen atoms clearly. Corrections have been made for temperature factor variations of different atoms and for the thermal anisotropy of the sodium ion. The tropolone ring deviates from a strictly planar form very slightly owing to some effect of the crystalline field. Bond lengths have been measured with standard deviations of 0·013 Å and can be explained both in terms of resonance structures and in terms of the molecular orbital method. Attention is drawn to the modified application of the inequality method and the comparison with the case of hydrochloride of tropolone.

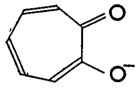
Introduction

Tropolone is a mother substance of the so-called tropoloid compounds with seven-membered carbon ring whose existence was predicted by Dewar (1945). The substance has been synthesized by Cook, Gibbs, Raphael & Sommerville (1950, 1951), Haworth & Hobson (1950, 1951), Doering & Knox (1950) and Nozoe, Seto, Kitahara, Kunori & Nakayama (1950) independently, although some derivatives of this substance were found before these dates in some natural products, for example, hinokitiol (Nozoe, 1936). Several interesting investigations of this substance were made by organic and physico-chemists cooperatively in this country, and from these results Nozoe has proposed a structure consisting of many resonance components with the three types, (*A*), (*B*) and (*C*). He concluded that the contribution from the structure with (*B*) is predominant (Nozoe, 1950). The same conclusion has been derived from molecular-orbital treatment by Kurita & Kubo (1951).

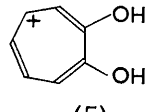

(*A*)


(*B*)


(*C*)


etc.

(*D*)


etc.

(*E*)

Tropolone is an amphoteric compound which is, on one side, a weak acid, giving, for example, a sodium salt with caustic soda, and, on the other, a base, giving a hydrochloride with hydrogen chloride gas. Nozoe (1950) has given the tropolonate anion and the tropolonium cation the resonance formulae (*D*) and (*E*), and has explained several reactions by these structures. In the case of tropolone, for example, cationoid replacement such as nitration occurs explosively unless the reaction temperature is kept low, but if concentrated sulphuric acid is added to the solution the rate of nitration becomes very slow. This is explicable by considering that tropolone becomes a cation in such strong acid solution in which carbon atoms in the nucleus have positive charges, and thus they repel a cationoid reagent.

According to Tsuboi (1952), the ultra-violet absorption spectra of tropolone itself, its anion and cation belong to one type, and that of tropolone methyl ether to another. From the theoretical point of view, the neutral tropolone, its anion and cation are isoelectronic with respect to the π-electron system, and the difference of the electronic states among them is chiefly due to the difference of the extent of the proton addition to the system. Thus it is of importance to tropoloid chemistry to carry out comparative determinations of crystal and molecular structures of these three compounds. Previously Sasada, Osaki & Nitta (1954) have reported the direct structure determination of tropolone hydrochloride by the inequality method. The present account describes the structure analysis of sodium tropolonate in detail.

It is also of special significance to examine whether or not the tropolone ring is really planar by using three-dimensional Fourier techniques, as several X-ray determinations of tropolone derivatives already reported have deduced its planarity from the projection on only one plane (Robertson, 1951; Campbell & Robertson, 1952; Taylor, 1952; Dunitz, 1952; Osaki & Nitta, 1952; Watanabé, 1952; Sasada, Osaki & Nitta, 1954; McDonald, 1955).

Experimental

Sodium tropolonate was prepared by dissolving tropolone in dilute sodium carbonate solution, and the first crystals obtained from it were somewhat deformed so that the *b* axis was curved in the plane perpendicular to the *c* axis. The crystals obtained by very slow recrystallization from aqueous solution were in the form of needles elongated along the *b* axis, and showed marked cleavage along the monoclinic (100) plane. It was therefore easy to obtain suitable crystals for rotation about the *b* and *c* axes. Crystallographic and physical data are:

Sodium tropolonate, $C_7H_5O_2Na$; monoclinic;
$a = 13{\cdot}91 \pm 0{\cdot}03$, $b = 3{\cdot}69 \pm 0{\cdot}02$, $c = 11{\cdot}67 \pm 0{\cdot}02$ Å, $\beta = 93{\cdot}1^\circ \pm 0{\cdot}5^\circ$.
Absent spectra: $(h0l)$ when l is odd, $(0k0)$ when k is odd.
Space group: $P2_1/c$–C^5_{2h}. Four formula units per unit cell.
Density (calc.) = $1{\cdot}600$ g.cm.$^{-3}$, density (obs.) = $1{\cdot}60$ g.cm.$^{-3}$.
Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 17{\cdot}58$ cm.$^{-1}$.

Using Cu $K\alpha$ radiation, oscillation photographs about the three principal axes were taken. These data were used in the preliminary determination of the crystal structure. For the precision measurement of the electron distribution in the crystal, a complete set of relative intensities for $(h0l)$, $(h1l)$ and $(h2l)$ were obtained by the Weissenberg procedure; the intensities for $(h3l)$ and $(h4l)$ were obtained from oscillation photographs alone. 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 4000 to 1. The crystals used have the following maximum and minimum dimensions at right angles to the axis of rotation:

Crystal 1: $0{\cdot}015 \times 0{\cdot}020$ cm.; Crystal 2: $0{\cdot}035 \times 0{\cdot}020$ cm.

The following two features were taken into account:

(1) The significant differences between intensities of the corresponding spectra on both sides of the central line of the Weissenberg photographs were recognized for reflexions with high values of h, and the elongation or contraction of the spectra was observed. By inspection, it was found that the ratio between the intensities of corresponding spectra on both sides of the central line increased with the value of h, and were nearly constant for the variation of l. From the analysis of the curves of intensity ratio with h and l, it was concluded that the crystal remained deformed as described above; and this was proved by the Weissenberg photographs about the *c* axis in which all reflexions were elongated uniformly. Correction was made for this deformation. However, the corrected values differ only slightly from those obtained by taking a simple average of the intensities of the corresponding spectra on both sides.

(2) Reflexions with indices (001), (103) and $(10\bar{3})$ were observed on Weissenberg photographs; these seem to be at variance with the space group indicated by the other reflexions. These spurious reflexions were explained as due to the double reflexions (Renninger, 1937) from the planes $(11\bar{1})$ and $(\bar{1}\bar{1}2)$, (112) and $(\bar{1}\bar{1}\bar{1})$; (111) and $(0\bar{1}2)$; $(11\bar{1})$ and $(0\bar{1}\bar{2})$, (112) and $(0\bar{1}\bar{5})$ respectively. As these spectra were of considerable intensity, the possibility that the intensities of some allowed reflexions may also be increased by double reflexion was considered. Fortunately it was found that most of the possible superpositions of double reflexions have negligible contributions. Only a few reflexions, to which contributions from the double reflexions might exceed slightly the limits of observational error, are shown in Table 2. As their number and magnitude are very small, however, this will not affect the subsequent analysis.

The corrections for polarization and Lorentz factors and for absorption were made in the usual way.

Application of the inequality method

The crystallographic data indicated that the molecules are packed in a very favourable way: the long *a* and the very short *b* axes clearly suggest that the molecules do not overlap, at least in the projections on (010), and are only slightly tilted with respect to the (010) plane. Therefore, it was to be expected that the approximate crystal structure might be revealed from the electron-density projection along the *b* axis. Thus the Harker–Kasper inequalities (1948), which were successful in the previous analysis of tropolone hydrochloride (Sasada *et al.*, 1954), were applied to the sign determination of the structure factors $(h0l)$, using Sakurai's chart (1952). The unitary structure factors were deduced from the relative values of $|F(h0l)|^2$, following the conventional procedure:

$$|U(h0l)|^2 = K^2|F(h0l)|^2 \exp 2B\,(\sin\theta/\lambda)^2/\hat{f}_0^{\,2}\,,$$

where $\hat{f}_0$ is the unitary scattering factor. The value of B was assumed to be $2{\cdot}00$ Å^2, and the scale factor K was chosen so that the average value of $U(h0l)^2$ was equal to

$$\Sigma z_i^2/(\Sigma z_i)^2 = 0{\cdot}046\,,$$

where z_i is the number of electrons in the ith atom. It was to be noticed that in this projection the unit cell was halved in the *c* direction, and for the sake of convenience the application of the inequality method was made for such a half cell, i.e. the above summation was made with all atoms in the half cell, the l indices being halved. By this procedure the signs of only six reflexions could be determined, if the sign of $(80\bar{8})$ was known. These are shown in column (*a*), Table 2, where ξ and η are the arbitrary parameters (Okaya & Nitta, 1952). An attempt was then made to estimate the signs of some more terms by raising the absolute magnitudes of the unitary structure factors. Such procedures were repeated with the unitary structure factors multiplied by an artificial constant, which was made to increase until some of the magnitudes of U contradicted the Harker–Kasper inequalities. As shown in column (*b*), Table 2, this method gave the signs of 46 out of 167 terms, b being imagined to be -1 by inspection. In spite of the artificial nature of this procedure the signs of only six terms had to be changed at later stages of refinement.

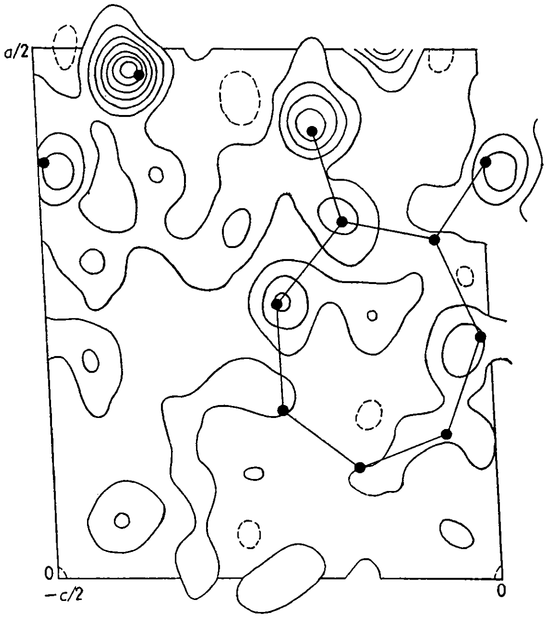


Fig. 1. First Fourier projection on (010) prepared with 46 terms whose signs were determined by the artificial inequality method taking $\xi = +1$, $\eta = -1$ and $b = -1$. The black circles show the final atomic positions.

The first Fourier map (Fig. 1), prepared with the 46 terms (taking $\xi = +1$, $\eta = -1$ and $b = -1$), showed significant peaks which were guessed to be sodium, two oxygen, two carbon atoms bonded to the oxygen, and some carbon atoms of the ring. From this map, and the shape of the tropolone ring revealed in the previous work, we derived approximate coordinates of each atom and computed the structure factors. The second Fourier projection already shows the crystal structure fairly well. Thus it may be concluded that even such very artificial procedures can give information on the crystal structure in some favourable circumstances. Further, it would also be interesting to compare the results of application of the inequalities to the present sodium salt with those to the hydrochloride of tropolone.

As stated above, signs of only six terms out of 167 could be directly determined in the former case, while the signs of 46 out of 83 reflexions could be determined in the latter, and its first Fourier projection already showed clearly the crystal structure. The mean value of U for the sodium salt was larger than that of the hydrochloride, though the plane symmetry of the projection in the latter was higher than that of the former. We have compared the distributions of magnitudes of the unitary structure factors in both cases (Fig. 2): the hydrochloride has a sharper distribution around the mean value. This may show that the magnitude distribution of the unitary structure factors, which is related to the characteristics of the distribution of atoms in the unit cell, plays some role in the successful application of this method, though the detailed interpretation is lacking.

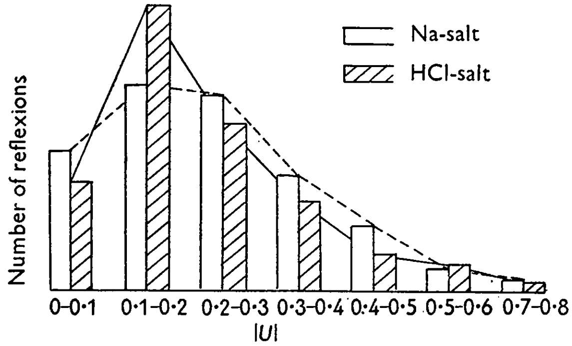


Fig. 2. Comparison between distributions of magnitudes of U in the sodium salt and in the hydrochloride of tropolone.

Refinement of the (010) projection and location of the hydrogen atoms

Starting from the approximate structure projected on the (010) plane mentioned in the last paragraph, successive Fourier projections were synthesized, until the value of $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ was reduced to 0·157. At this stage, the (F_o-F_c) syntheses on the (010) plane were applied. The corrections for the atomic coordinates were estimated from the equation

$$\Delta r = (dD/dr)_{r=0}/2p\varrho(0)\,,$$

where $\varrho(0)$ is the electron density at an atomic centre and p is a constant, whose value was deduced from the fourth Fourier map assuming the electron density near an atomic centre to be represented by the equation

$$\varrho(r) = \varrho(0)\exp\left[-pr^2\right].$$

In the structure-factor calculation, the atomic scattering factors were taken from McWeeny (1951), using for oxygen $\bar{f}_{\rm O} = \frac{1}{3}(f^{\parallel}+2f^{\perp})$, and for carbon the values for 'valence states'. In the final calculation, the atomic scattering factor for oxygen was modified by the equation

$$\bar{f}'_{\rm O} = \bar{f}_{\rm O}+\tfrac{1}{4}(f_{{\rm O}^{-2}}-f_{\rm O})\,,$$

where $f_{{\rm O}^{-2}}$ and $f_{\rm O}$ are the atomic scattering factors for $\rm O^{-2}$ and O tabulated in the *International Tables* (1935).

It was observed from the $(\varrho_o-\varrho_c)$ maps that the thermal vibrations of the atoms were approximately isotropic except for the sodium ion, and each atom in the tropolone ring had almost the same value for the

B factor so far as the projection was concerned. Thus in the assignment of B parameters, proceeding simultaneously with the refinement of atomic coordinates, the sodium ion and the tropolone ring were treated separately. Though the small fluctuations of the magnitudes of thermal motions among individual atoms in the tropolone ring were observed, the mean values of B for oxygen and carbon atoms were employed for convenience. The best B factors deduced from the eighth $(\varrho_o - \varrho_c)$ map were 2·63 Å^2 for oxygen and 2·53 Å^2 for carbon and hydrogen.

The sodium ion showed marked thermal anisotropy, and consequently scattering factors of the form $f = f_0 \exp\left[-\{\alpha + \beta \sin^2(\varphi - \psi_a)\}(\sin\theta/\lambda)^2\right]$ were employed for this ion (Hughes, 1941; Cochran, 1951). In this expression α and β are constants, ψ_a is the angle between the direction of maximum vibration and the a axis, and $(2\sin\theta, \varphi)$ are the polar coordinates of a point in the $(h0l)$ section of the reciprocal lattice, φ being measured from the c^* axis. Assuming that the electron density for the whole sodium ion were represented by the equation

$$\varrho(r) = \varrho(0) \exp\left[-pr^2\right],$$

so that the scattering factor for the sodium ion had the Gaussian form, the value of α and β were determined without tedious procedure. This assumption will not introduce any serious error for the values of α and β in the case where the degree of anisotropy is not large. The final values of α, β and ψ_a were 2·10, 0·46 and 0° respectively. The final Fourier projection on the (010) plane and the ninth $(\varrho_o - \varrho_c)$ map are shown in Fig. 3. The significant peaks on the latter are evidently due to the hydrogen atoms.

At this stage the R index decreased to 0·084, including the contributions from hydrogen atoms placed radially at a distance of 1·0 Å from the carbon atoms. In Table 1 are listed the final atomic coordinates and in Table 2 observed and calculated structure factors.

Table 1. *Atomic coordinates*

Atom	x/a	z/c	y/b	X' (Å)	Z' (Å)	Y (Å)
Na	0·4732	0·1187	0·333	6·507	1·383	1·229
O_1	0·3948	0·0067	−0·204	5·488	0·078	−0·753
O_2	0·4210	−0·1894	0·132	5·976	−2·207	0·487
C_1	0·3190	−0·0522	−0·112	4·470	−0·608	−0·413
C_2	0·3344	−0·1606	0·078	4·753	−1·871	0·288
C_3	0·2592	−0·2390	0·210	3·756	−2·784	0·775
C_4	0·1602	−0·2372	0·207	2·378	−2·763	0·764
C_5	0·1028	−0·1529	0·041	1·526	−1·781	0·151
C_6	0·1345	−0·0530	−0·120	1·904	−0·617	−0·443
C_7	0·2279	−0·0082	−0·196	3·175	−0·096	−0·723

Determination of the *y* coordinates

We next attempted to estimate the y coordinate of each atom. The structure analysis already reported and much physical evidence have shown that the tropolone ring is a planar regular heptagon. In the present work, we have assumed this, so that, by fitting an ellipse on the seven carbon atoms, the inclination of the tropolone ring was determined to be about 26° from the (010) plane, the plane of the ring being

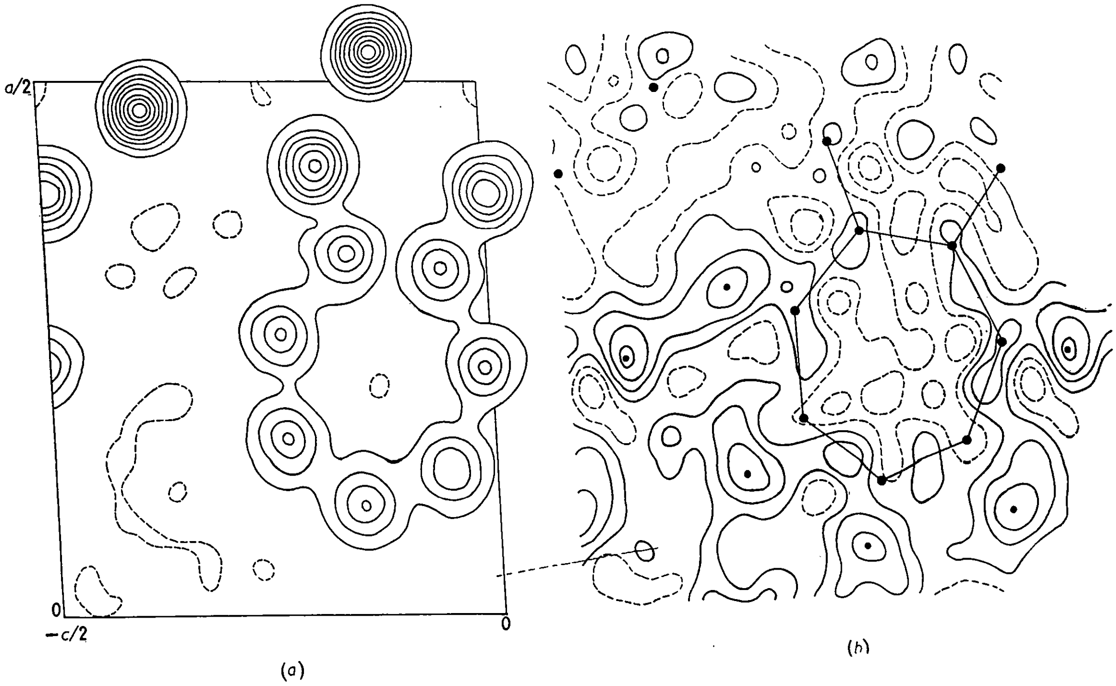


Fig. 3. (a) The final Fourier projection on (010). Contours at intervals of 2 e.Å^{-2} with the lowest solid contour at 2 e.Å^{-2}. The zero contour is broken. (b) The final $(F_o - F_c)$ projection on (010). Contours at intervals of 0·2 e.Å^{-2} with the lowest solid contour at 0·2 e.Å^{-2}.

nearly parallel to the a axis. This inclination and the presence of the c glide imposed severe limitation on the height of the molecular plane.

In the (010) projection there is no distinction between the centre of symmetry and the screw axis, and consequently there are two alternative assignments of these symmetry elements. The stable position of the sodium ion surrounded by six oxygen atoms was considered for these two cases, and Fourier projections along the a axis were calculated. Only one of them gave a reasonable pattern. Thus we carried on further refinements of the y coordinates on the basis of this arrangement. The final Fourier projections along the c and a axes are shown in Fig. 4. The best y coordinates were determined by the three-dimensional line syntheses through atomic centres corrected for the termination errors by means of the back-shifts (Booth, 1946).

In the calculation of the structure factors for $(hk0)$, $(0kl)$ and (hkl), McWeeny's atomic scattering factors with a mean B value were used, the value of B being 3·20 Å^2, and the contributions from hydrogen atoms were omitted. The R indices for $(hk0)$, $(0kl)$ and (hkl) were 0·130, 0·157 and 0·134 respectively, if unobserved reflexions were neglected (Table 3*).

---

* Table 3 has been deposited as Document No. 4736 with the ADI Auxiliary, Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1·25 for photoprints, or $1·25 for 35 mm. microfilm. Advance payment is required. Make cheques of money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 2. *Observed and calculated structure factors $F(h0l)$, with signs determined by the inequality method*

			Sign	
hkl	F_o	F_c	(a)	(b)
000	—	148		
100	30·4	−28·7		$b\xi$
200	6·1	−6·8		
300	16·6	−14·9		
400	13·7	−13·8		
500	7·9	−6·6		
600	5·6	−5·3		
700	7·3	7·0		$b\xi$
800	6·5	6·4		
900	4·0	3·6		
10,0,0	< 0·6	0·2		
11,0,0	8·6	−8·4		
12,0,0	5·4	5·5		
13,0,0	2·8*	3·4		
14,0,0	6·2	−6·5		
15,0,0	4·0	4·2		
16,0,0	3·9	−4·5		
17,0,0	< 0·6	0·7		
002	2·8	3·4		
004	12·9	12·3		
006	13·3	12·5		
008	10·7	10·5		
0,0,10	< 1·0	−1·4		
0,0,12	1·2	1·0		
0,0,14	1·1	−0·9		η
102	20·9	20·7		
202	2·2*	1·6		
302	14·6	15·2		$\xi\eta$
402	11·1	10·7		
502	12·5	−12·5		
602	2·2	3·0		
702	20·8	−20·6	$\xi\eta$	$\xi\eta$
802	13·3	13·5		
902	11·3	−10·8		
10,0,2	23·0	22·9		$b\eta$
11,0,2	17·2	−17·4		$\xi\eta$
12,0,2	< 1·0	−1·3		
13,0,2	6·1	6·3		
14,0,2	< 1·0	−0·4		
15,0,2	< 0·8	0·7		
16,0,2	1·5	1·9		
17,0,2	< 0·4	−0·5		
$10\bar{2}$	30·9	−32·7		
$20\bar{2}$	4·1	−4·1		
$30\bar{2}$	3·3	−3·1		
$40\bar{2}$	21·7	−20·8		
$50\bar{2}$	23·4	22·7		
$60\bar{2}$	1·9	−2·3		
$70\bar{2}$	1·0*	0·2		
$80\bar{2}$	2·5	−2·3		
$90\bar{2}$	15·6	14·8		
$10,0,\bar{2}$	11·2	−10·0		η
$11,0,\bar{2}$	1·3	1·5		$b\xi\eta$
$12,0,\bar{2}$	13·5	−13·9	$a\eta$	η
$13,0,\bar{2}$	7·6	8·1		$b\xi\eta$
$14,0,\bar{2}$	1·9	−2·4		
$15,0,\bar{2}$	3·7	4·1		
$16,0,\bar{2}$	< 0·6	−0·2		η
$17,0,\bar{2}$	< 0·4	1·3		
104	4·2*	4·0		
204	16·5	−15·4		
304	7·3	−7·5		
404	< 1·0	1·0		
504	14·0	13·2		
604	16·9	−16·2		
704	11·8	10·9		
804	3·7	3·3		
904	5·0	−4·3		
10,0,4	< 1·0	0·1		
11,0,4	2·6	−2·7		
12,0,4	< 0·8	−0·8		
13,0,4	1·0	−1·9		
14,0,4	2·9	3·3		
15,0,4	3·3	−4·1		
16,0,4	4·3	4·4		
$10\bar{4}$	14·6	14·3		ξ
$20\bar{4}$	43·8	−41·8		b
$30\bar{4}$	22·1	21·7	ξ	ξ
$40\bar{4}$	19·5	−19·7		b
$50\bar{4}$	34·5	34·4	$a\xi$	ξ
$60\bar{4}$	11·5	−11·4		b
$70\bar{4}$	4·8	6·0		ξ
$80\bar{4}$	4·4	4·9		
$90\bar{4}$	12·1	−12·6		
$10,0,\bar{4}$	< 1·0	−1·9		
$11,0,\bar{4}$	9·0	−9·2		
$12,0,\bar{4}$	7·1	8·3		
$13,0,\bar{4}$	6·5	7·3		
$14,0,\bar{4}$	< 1·0	−0·0		
$15,0,\bar{4}$	< 1·0	0·9		
$16,0,\bar{4}$	< 0·8	−0·6		
$17,0,\bar{4}$	3·9	−4·6		
106	6·2	5·1		
206	< 0·8	−0·7		
306	15·3*	15·6		$b\xi\eta$
406	22·6	−22·0		η
506	16·1	16·3		$b\xi\eta$
606	23·0	−22·9	η	η
706	5·5	5·4		$b\xi\eta$
806	2·8*	−3·6		η
906	11·7	11·8		$b\xi\eta$
10,0,6	6·1	6·1		
11,0,6	2·8	−2·8		
12,0,6	4·7	−5·3		
13,0,6	< 0·8	1·1		
14,0,6	2·7	−3·0		
15,0,6	< 0·4	0·8		
16,0,6	2·3	−2·7		
$10\bar{6}$	22·1	−20·6		
$20\bar{6}$	10·3	10·6		
$30\bar{6}$	3·7	3·6		
$40\bar{6}$	< 1·0	0·4		
$50\bar{6}$	1·4	2·3		
$60\bar{6}$	1·8	1·3		
$70\bar{6}$	14·8	−14·6		
$80\bar{6}$	< 1·0	2·0		
$90\bar{6}$	< 1·0	−0·9		
$10,0,\bar{6}$	7·5	8·5		
$11,0,\bar{6}$	5·3	−5·2		
$12,0,\bar{6}$	8·5	7·7		
$13,0,\bar{6}$	3·6	−3·8		
$14,0,\bar{6}$	3·0*	2·3		$b\eta$
$15,0,\bar{6}$	2·9	−3·2		$\xi\eta$
$16,0,\bar{6}$	1·5	−1·6		
108	< 1·0	−2·1		
208	3·6	4·0		
308	7·1	−6·3		
408	15·1	14·5		
508	< 1·0	−1·2		
608	5·0	−4·4		
708	2·2	−3·8		
808	< 1·0	−1·6		
908	5·5	−4·8		
10,0,8	2·1	2·7		
11,0,8	5·4	5·9		

Table 2 (*cont.*)

hkl	F_o	F_c	Sign (*a*)	Sign (*b*)
12,0,8	< 0·8	− 1·6		
13,0,8	6·9	5·9		ξ
14,0,8	4·8	− 4·9		b
$10\bar{8}$	11·4	−11·0		
$20\bar{8}$	2·6	2·7		
$30\bar{8}$	13·6	−12·8		
$40\bar{8}$	5·8	5·0		
$50\bar{8}$	< 1·2	1·6		$b\xi$
$60\bar{8}$	3·9	4·3		
$70\bar{8}$	12·2	−10·8		$b\xi$
$80\bar{8}$	17·9	16·7	a	+1
$90\bar{8}$	6·7	− 6·7		
$10,0,\bar{8}$	3·9	− 4·7		
$11,0,\bar{8}$	1·5*	1·9		
$12,0,\bar{8}$	< 1·0	− 0·8		
$13,0,\bar{8}$	3·8	3·8		
$14,0,\bar{8}$	3·2	− 3·4		
$15,0,\bar{8}$	1·0	0·8		
1,0,10	9·2	− 9·6		$\xi\eta$
2,0,10	16·1	13·9		$b\eta$
3,0,10	12·5	−10·4		$\xi\eta$
4,0,10	5·0	6·8		$b\eta$
5,0,10	7·2	6·3		
6,0,10	2·1	− 1·8		
7,0,10	5·5	− 6·0		
8,0,10	4·6	3·9		
9,0,10	2·5	− 3·1		
10,0,10	3·2	3·3		
11,0,10	4·8	− 4·2		
12,0,10	< 0·4	0·1		
$1,0,\overline{10}$	8·5	− 8·3		$\xi\eta$
$2,0,\overline{10}$	< 1·0	− 0·3		
$3,0,\overline{10}$	7·1	6·9		
$4,0,\overline{10}$	< 1·0	1·3		
$5,0,\overline{10}$	12·2	11·8		$\xi\eta$
$6,0,\overline{10}$	12·0	−10·4		
$7,0,\overline{10}$	2·3	2·0		
$8,0,\overline{10}$	4·0	− 4·3		
$9,0,\overline{10}$	1·3	− 1·8		
$10,0,\overline{10}$	2·7	2·2		
$11,0,\overline{10}$	1·9	2·7		
$12,0,\overline{10}$	4·6	− 3·9		
$13,0,\overline{10}$	4·9	3·8		
1,0,12	1·2	− 1·7		
2,0,12	7·4	− 7·5		+1
3,0,12	2·8	2·4		
4,0,12	5·1	− 4·7		
5,0,12	8·0	7·2		$b\xi$
6,0,12	< 1·0	− 0·0		
7,0,12	1·8	− 2·1		
8,0,12	2·0	2·1		
9,0,12	3·5	− 3·2		$b\xi$
10,0,12	1·0	2·1		
$1,0,\overline{12}$	7·9	8·0		
$2,0,\overline{12}$	4·4	− 3·9		
$3,0,\overline{12}$	4·6	5·3		
$4,0,\overline{12}$	< 1·0	− 0·9		
$5,0,\overline{12}$	1·8	1·5		
$6,0,\overline{12}$	9·1	− 8·2		
$7,0,\overline{12}$	< 1·0	0·6		
$8,0,\overline{12}$	< 1·0	0·2		
$9,0,\overline{12}$	3·8	2·9		
$10,0,\overline{12}$	3·2	− 2·2		b
$11,0,\overline{12}$	0·8	1·3		
1,0,14	4·2	3·6		$b\eta$
2,0,14	< 0·6	0·3		
3,0,14	< 0·6	− 0·1		
4,0,14	2·0	− 2·4		
5,0,14	4·2	3·5		
$1,0,\overline{14}$	< 0·6	0·1		
$2,0,\overline{14}$	3·3	− 2·9		η
$3,0,\overline{14}$	4·3	3·2		$b\xi\eta$
$4,0,\overline{14}$	< 0·6	− 1·5		
$5,0,\overline{14}$	< 0·6	− 0·8		
$6,0,\overline{14}$	< 0·6	− 0·5		
$7,0,\overline{14}$	3·7	− 3·3		

* Reflexion whose intensity might be increased by superposition of double reflexion.

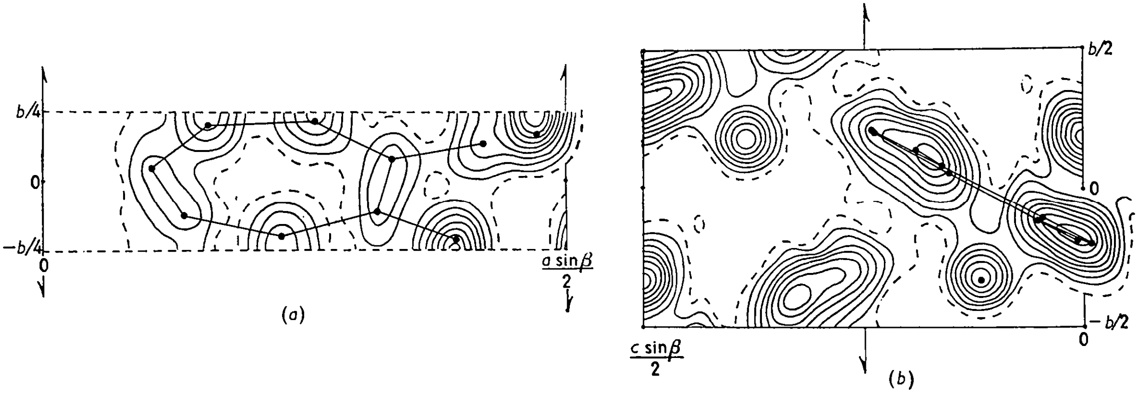


Fig. 4. The final Fourier projections (*a*) on (001), (*b*) on (100). Contours at intervals of 2 e.Å^{-2}, that at 4 e.Å^{-2} being broken. Black circles show the final atomic positions.

Coordinates and molecular dimensions

The final coordinates of the carbon, oxygen and sodium atoms are shown in Table 1. The coordinates x, y and z are referred to the monoclinic crystal axes with the origin at the centre of symmetry. The coordinates X', Y and Z' are referred to orthogonal axes a, b and c', c' being taken perpendicular to the a and b crystal axes, so that

$$X' = X+Z\cos\beta, \quad \text{and} \quad Z' = Z\sin\beta\,,$$

where $X = x$ and $Z = z$.

It was found that the coordinates of the ring atoms $O_1, \ldots, C_7$ could be fitted to an equation of the form

$$Y = AX'+BZ'+C\,.$$

A, B and C, which give the precise indication of the plane of the ring, were determined by the method of least squares to be 0·0162, −0·5499 and −0·8182

Table 4. *Deviations from the mean plane*

Atom	$Y_{\text{obs.}}$ (Å)	$Y_{\text{calc.}}$ (Å)	Δ (Å)	Displacement from plane (Å)
O_1	−0·753	−0·772	0·019	0·017
O_2	0·487	0·492	−0·005	−0·005
C_1	−0·413	−0·412	−0·001	−0·001
C_2	0·288	0·288	0·000	0·000
C_3	0·775	0·774	0·001	0·001
C_4	0·764	0·740	0·024	0·021
C_5	0·151	0·186	−0·035	−0·031
C_6	−0·443	−0·448	0·005	0·004
C_7	−0·723	−0·714	−0·009	−0·008

respectively. The deviations Δ of the two series of Y coordinates, as derived from the three-dimensional line syntheses and as calculated by means of the above equation, are shown in Table 4. The average deviation 0·011 Å between the corresponding values of Y for the ring atoms is of course only slightly greater than the average perpendicular displacement 0·010 Å from this mean plane of the ring directly calculated (last column of Table 4).

The bond lengths and valency angles in the tropolone ring are shown in Fig. 5. In this calculation the $Y_{\text{calc.}}$ values of the ring atoms were employed instead of those given in Table 1. These do not differ significantly from the observed values, and are likely to be more reliable.

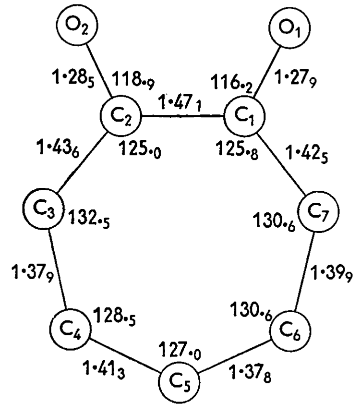


Fig. 5. Bond lengths (Å) and bond angles (°).

The estimated positions of the hydrogen atoms are given in Table 5, the Y coordinates being obtained by substituting the estimated X' and Z' values in the equation of the mean plane of the ring, although the assumed positions were used in the calculations of the $(h0l)$ structure factors.

Table 5. *Hydrogen coordinates and bond lengths of* C–H

Atom	X' (Å)	Z' (Å)	Y (Å)
$H(C_3)$	4·15	−3·65	1·26
$H(C_4)$	1·72	−3·56	1·17
$H(C_5)$	0·70	−2·01	0·30
$H(C_6)$	1·02	−0·07	−0·76
$H(C_7)$	2·99	0·79	−1·20

$H–C_3 = 1{\cdot}07$, $H–C_4 = 1{\cdot}12$, $H–C_5 = 0{\cdot}87$, $H–C_6 = 1{\cdot}08$, $H–C_7 = 1{\cdot}03$ Å.

Estimation of accuracy

The standard deviations of the atomic coordinates, $\sigma(x)$, etc., were estimated by the method of Cruickshank (Cruickshank, 1949, 1954; Ahmed & Cruickshank, 1953), where

$$\sigma(x) = \frac{1}{A}\frac{2\pi}{a}\{\Sigma h^2(\Delta F)^2\}^{\frac{1}{2}} \Big/ \left|\frac{\partial^2\varrho}{\partial x^2}\right| ,$$

and

$$\sigma(y) = \frac{1}{V}\frac{2\pi}{b}\{\Sigma k^2(\Delta F)^2\}^{\frac{1}{2}} \Big/ \left|\frac{\partial^2\varrho}{\partial y^2}\right| .$$

In these equations, A is the area of the cell projection, V the volume of the cell, ΔF the error in F value, and $\partial^2\varrho/\partial x^2$, etc. the curvatures of the electronic density at the atomic centres. In evaluating this expression we have taken $\Delta F = F_o - F_c$, because the main finite-series errors should have been eliminated by the difference-syntheses methods employed (Cochran, 1951). 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

$$\partial^2\varrho/\partial x^2 = -2p\varrho(0) .$$

The constant p was evaluated by graphical plots of $\log \varrho$ against r^2 from the final F_o synthesis.

The coordinate standard deviations obtained by these methods were:

$\sigma(x) = \sigma(z) = 0{\cdot}003$ Å, $\sigma(y) = 0{\cdot}006$ Å for sodium;
$\sigma(x) = \sigma(z) = 0{\cdot}006$ Å, $\sigma(y) = 0{\cdot}012$ Å for oxygen;
$\sigma(x) = \sigma(z) = 0{\cdot}009$ Å, $\sigma(y) = 0{\cdot}016$ Å for carbon.

From these results the standard deviation of a C–C bond comes out to be about 0·013 Å, and that of a C–O bond about 0·011 Å. The standard deviation of bond angles computed by the equation given by Ahmed & Cruickshank (1953) was found to be 0·9°. The standard deviation of electron density, given by

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

was found to be 0·18 e.Å^{-2} for the (010) projection.

Discussion

The crystal structure projected on (010) is shown in Fig. 6. The sodium ion has six oxygen neighbours with Na–O distances from 2·37 to 2·60 Å. Short intermolecular C–C distances are shown in Fig. 6.

It was observed from the ninth $(F_o - F_c)$ map that the values of $(\varrho_o - \varrho_c)$ at the atomic centres are negative for C_4, C_5 and C_6 and positive for C_1, C_2, C_3 and C_7. Since the standard deviation of electron density is 0·18 e.Å^{-2}, such differences are probably significant, and this will mean that the thermal vibration of each carbon atom in the ring increases with increasing distance of the atom from the sodium ion. The relative arrangement of tropolone ring and sodium ion, which is of the type found in ordinary organic salt crystals, will reasonably explain this on the one hand and the anisotropic vibration of the sodium ion on the other. It is also compatible with the observed cleavage along the (100) plane.

We now discuss the molecular structure of the tropolonate anion. As stated previously, it is of significance to examine the planarity of the tropolone ring. The displacements of the carbon atoms from the mean plane of the tropolone ring vary from zero to 0·021 Å except for C_5 (Table 4). Owing to relatively large standard deviations of the y coordinates, these deviations are not significant. For C_5, however, the displacement amounts to 0·031 Å, and is only possibly significant. In such a case it might be concluded that the tropolone ring deviates from a strictly planar form very slightly owing to some effect of crystalline field or other factors. In the following discussion we take the bond lengths and angles calculated from the assumption of the planarity of the ring rather than the observed ones, differences between them being not significant.

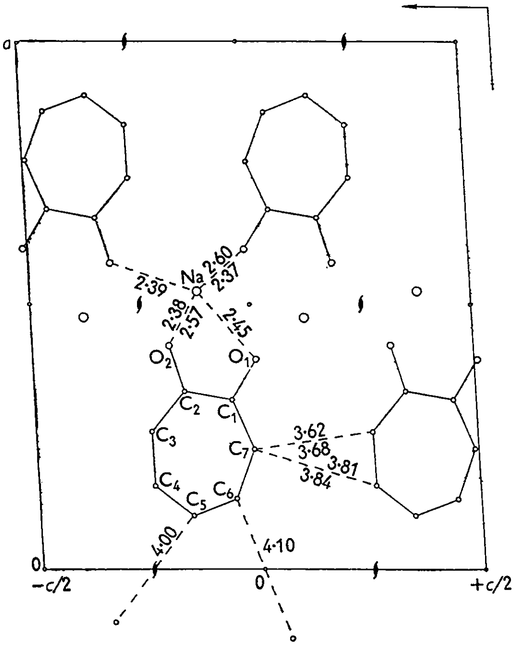


Fig. 6. Arrangement of molecules in the (010) projection.

Whether all the C–C bond lengths in a tropolone ring are equal or not is an interesting point. By the significant tests it was concluded that the bond C_1–C_2 differs from the others and that C_2–C_3 and C_7–C_1 differ from C_3–C_4 and C_5–C_6 significantly.

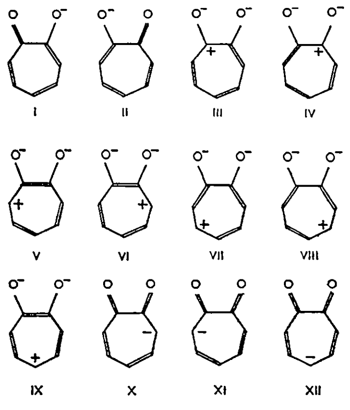


Fig. 7. Canonical formulae of tropolonate anion.

The canonical formulae of the Kekulé type with formal charges are shown in Fig. 7. In terms of the resonance theory, the bond lengths observed will imply that in the actual ground state the contributions, besides the main resonance components of the type *A* (I and II), from the structures of the type *B* (III–IX) rather than the type *C* (X–XII) should be considered to be appreciable. It might be added that, owing to some crystalline field effect, e.g. electrostatic interaction with the sodium ion as well as the neighbouring tropolone ring with some uneven charge distribution, the contributions from III–VI and X might become greater, so that the mirror symmetry perpendicular to the molecular plane through C_5 and the mid-point of C_1–C_2 could be lost. The fact that in the *D* map shown in Fig. 3(*b*) the value of $(\varrho_o-\varrho_c)$ at the centre of C_7 is significantly larger than the others might give partial support to this argument.

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

I–II, 20%; III–VI, 7%; VII–IX, 3%; X, 15%; and XI–XII, 4%,

the relation

$$R = R_1-(R_1-R_2)3x/(2x+1)$$

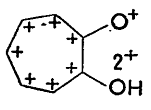
being used with $R_1 = 1{\cdot}54$ Å (C–C), $R_2 = 1{\cdot}34$ Å (C=C), and $R_1 = 1{\cdot}42$ Å (C–O), $R_2 = 1{\cdot}20$ Å (C=O) (Pauling, 1948).

The result is also compatible with that of the molecular orbital calculation, although in this case the mirror perpendicular to the molecular plane through C_5 and the mid-point of the C_1–C_2 bond was assumed in the treatment (Kurita & Kubo, 1951). For example, the bond lengths, the charge distribution and the direction of the molecular dipole moment (Fig. 7), and some other chemical evidence summarized by Nozoe (1950) and by Kubo, Kurita & Kimura (1954), are in good agreement with the above conclusion.

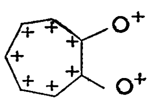
The electron-diffraction investigation of the neutral tropolone by Kimura & Kubo (1953), in which special attention was paid to the C–O distances, has shown that the best agreement between the whole theoretical intensity curve and that observed was obtained when the lengths of the C–O bonds were taken to be 1·34 and 1·26 Å. On the other hand, the distances of the C–O bonds are 1·42 and 1·40 Å in tropolone hydrochloride (Sasada, Osaki & Nitta, 1954), which are not yet the final values (refinements are in progress). Taking the average of the two C–O distances in each case, it was observed that

C–O (anion) < C–O (neutral) < C–O (cation).

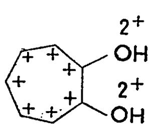
If the ten π-electrons are removed from tropolone, its anion and cation, the effective core charges become as follows:



(a)



(b)



(c)

In (*a*), the formal charge on each oxygen atom is more approximately described by putting $+1{\cdot}5$ if the resonance and hydrogen-bond formation are considered. When the charges on oxygen atoms are reduced to $+1$ from $+1{\cdot}5$, the case (*b*), it corresponds to the decrease of the electronegativity of oxygen; the polarity of the C–O bond is reduced and the bond order increases, i.e. the bond lengths are contracted. In (*c*), on the other hand, the charges on oxygen atoms are increased to $+2$ from $+1{\cdot}5$. The electronegativity of oxygen, bond polarity and bond order of the C–O bond therefore change in the reverse direction compared with (*b*), i.e. the C–O lengths are increased.

With regard to the positions of the hydrogen atoms, the average value of the C–H bond lengths (Table 5) is 1·03 Å. This agrees well with 1·03 Å found in α-pyridone (Penfold, 1953), although it is considerably greater than the values found in salicylic acid (Cochran, 1953) and benzoic acid (Sim, Robertson & Goodwin, 1955). The estimated electron content within each hydrogen atom varies from $0{\cdot}8_5$ to 1·1. However, it is less significant to make precise comparison with other analyses because of relatively large errors in the map and of ambiguity in drawing the boundary of each hydrogen atom.

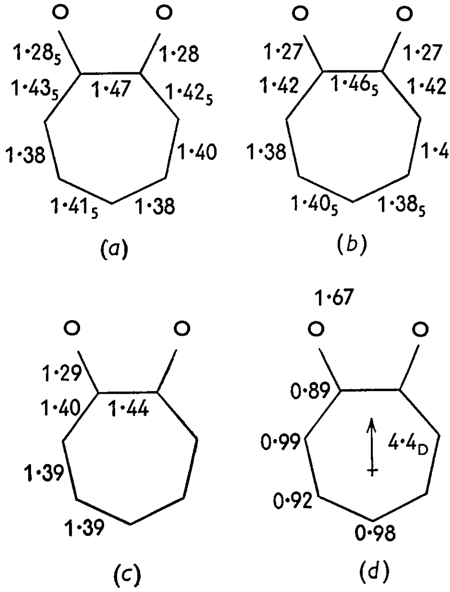


Fig. 8. (*a*) Observed bond lengths. (*b*) Bond lengths calculated, using Pauling's relation. (*c*) Results of molecular-orbital treatment (Kurita & Kubo, 1951). (*d*) π-Electron distribution.

Finally, attention was paid to values of $(\varrho_o-\varrho_c)$ at the mid-points of the C–C bonds in the map shown in Fig. 3(*b*). Of course nothing definite can be concluded about the charge distribution of bonding electrons between carbon atoms, unless appropriate corrections for the anisotropic thermal vibrations of carbon atoms are made. Still it seems significant that the charge distribution between C_1–C_2 is much less than for the other C–C pairs, corresponding to the explanation of the C–C bond lengths on the basis of the resonance theory.

We wish to express our thanks to Prof. T. Nozoe and his collaborators for supplying the sample and also for continued encouragement. We are also indebted to those who have been making the cooperative physicochemical investigations of 'tropolone chemistry' in this country for their helpful discussions. The cost of this research has been defrayed from the Grant in Aid for Fundamental Scientific Research from the Ministry of Education.

References

Ahmed, F. R. & Cruickshank, D. W. J. (1953). *Acta Cryst.* **6**, 385.

Booth, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.

Campbell, R. B. & Robertson, J. M. (1952). *Chem. Ind.* p. 1266.

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

Cochran, W. (1953). *Acta Cryst.* **6**, 260.

Cook, J. W., Gibbs, A. R., Raphael, R. A. & Sommerville, A. R. (1950). *Chem. Ind.* p. 427.

Cook, J. W., Gibbs, A. R., Raphael, R. A. & Sommerville, A. R. (1951). *J. Chem. Soc.* p. 1266.

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

Cruickshank, D. W. J. (1954). *Acta Cryst.* **7**, 519.

Dewar, M. J. S. (1945). *Nature, Lond.* **155**, 50.

Doering, W. E. & Knox, L. H. (1950). *J. Amer. Chem. Soc.* **72**, 2305.

Dunitz, J. D. (1952). *Nature, Lond.* **169**, 1087.

Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.

Haworth, R. D. & Hobson, J. D. (1950). *Chem. Ind.* p. 441.

Haworth, R. D. & Hobson, J. D. (1951). *J. Chem. Soc.* p. 561.

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

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

Kimura, M. & Kubo, M. (1953). *Bull. Chem. Soc. Japan*, **26**, 250.

Kubo, M., Kurita, Y. & Kimura, M. (1954). *Molecular Structure and Related Problems*. Monograph Series of the Research Institute of Applied Electricity, No. 4, p. 1.

Kurita, Y. & Kubo, M. (1951). *Bull. Chem. Soc. Japan*, **24**, 13.

McDonald, T. R. R. (1955). *Acta Cryst.* **8**, 61.

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

Nozoe, T. (1936). *Bull. Chem. Soc. Japan*, **11**, 295.

Nozoe, T. (1950). *Proc. Japan Acad.* **26**, No. 9, 30.

Nozoe, T., Seto, S., Kitahara, Y., Kunori, M. & Nakayama, Y. (1950). *Proc. Japan Acad.* **26**, No. 7, 38.

Okaya, Y. & Nitta, I. (1952). *Acta Cryst.* **5**, 564.

OSAKI, K. & NITTA, I. (1952). Unpublished.
PAULING, L. (1948). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.
PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 591.
RENNINGER, M. (1937). *Z. Kristallogr.* **97**, 107.
ROBERTSON, J. M. (1951). *J. Chem. Soc.* p. 1222.
SAKURAI, K. (1952). *Acta Cryst.* **5**, 546.
SASADA, Y., OSAKI, K. & NITTA, I. (1954). *Acta Cryst.* **7**, 113.
SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157.
TAYLOR, C. A. (1952). *Nature, Lond.* **169**, 1087.
TSUBOI, M. (1952). *Bull. Chem. Soc. Japan*, **25**, 369.
WATANABÉ, T. (1952). Unpublished.

Acta Cryst. (1956). **9**, 214

The Crystal Structure of the Intermetallic Compound $Mg_6Si_7Cu_{16}$*

BY GUNNAR BERGMAN AND JOHN L. T. WAUGH

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena 4, California, U.S.A.

(*Received* 1 *August* 1955)

The earlier reported atomic positions in the structure of the intermetallic compound $Mg_6Si_7Cu_{16}$ (Bergman & Waugh) have been refined on the basis of single-crystal intensity data by application of a least-squares procedure. The atomic positions are essentially the same as those obtained by Nagorsen & Witte in an independent investigation, with the exception of the magnesium positions, which differ significantly. As Nagorsen & Witte used a semiquantitative procedure with successive adjustments of the positional parameters it may perhaps be concluded that the results presented here are more reliable. This conclusion is supported by the fact that the new positions correspond to better packing of the atoms.

The derivation of the trial structure demonstrates that no other atomic arrangement is possible even when intensity data are completely disregarded, provided that normal packing conditions exist.

Introduction

In an earlier paper (Bergman & Waugh, 1953) the determination of the crystal structure of the compound $Mg_6Si_7Cu_{16}$ was described briefly. Atomic positions in an early stage of refinement were given and it was intended to publish a detailed report on this structure determination with refined positional parameters at a later time. However, shortly after this paper had been published a paper (Nagorsen & Witte, 1953) describing an independent structure determination of the same compound appeared. The present paper will therefore consist largely of comparisons of the methods and results in the two investigations.

Experimental work

Preparation of the compound and isolation of single crystals

In order to avoid difficulties associated with the relatively high volatility of magnesium, a copper–silicon alloy was first prepared by melting the elements† in a sealed evacuated quartz tube in the atomic proportions 16:7. The relatively low-melting copper–silicon alloy was then melted with magnesium metal† in a sealed evacuated quartz tube to form an alloy of the composition $Mg_6Si_7Cu_{16}$. Good mixing was secured by vigorous shaking of the tube. The alloy was next allowed to cool to room temperature at a cooling rate of about 20° C. per hour. When the alloy pellet was broken up a large number of well developed crystals of octahedral habit and blue-grey color could be isolated.

Laue symmetry and unit-cell dimensions

The octahedral crystals showed Laue symmetry O_h–$m3m$. On the basis of rotation and Weissenberg photographs (rotation about [100]) it was established that the crystals have a face-centered cubic lattice with a cell constant approximately equal to 11·65 Å. These results agreed with those reported by Witte (1938) for the phase $Mg_6Si_7Cu_{16}$ in his preliminary investigation of this phase (a_0 = 11·67 Å). A refinement of the lattice parameter was not carried out as Witte's result was considered sufficiently accurate. Nagorsen & Witte (1953) report the parameter value 11·65 ±0·02 Å in their joint paper.

Diffraction intensity data

As the structure has cubic symmetry diffraction intensity data for the (*hk*0) reflections were sufficient for the refinement of the structure. These data were obtained by Weissenberg photography (Cu *Kα* radiation) with application of the multiple-film technique of de Lange, Robertson & Woodward (1939) and Robertson (1943).

---

* Contribution No. 2078 from the Gates and Crellin Laboratories.

† The materials used in this preparation were all of at least 99·9 % purity.