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The Crystal and Molecular Structure of Tropolone

By Hirotaka Shimanouchi and Yoshio Sasada

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, *Japan*

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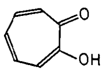
Tropolone, $C_7H_6O_2$, crystallizes in space group $P2_1/c$, with $a=7{\cdot}135$, $b=12{\cdot}178$, $c=7{\cdot}122$ Å, $\beta=99{\cdot}63°$ and $Z=4$. The crystal structure was solved by the symbolic addition procedure and refined by the least-squares method to give the final R value of 0·054 for the 853 observed reflexions. The molecule is essentially planar and exhibits a slight degree of bond alternation in the seven-membered ring. The hydroxyl group makes a bifurcated hydrogen bond with carbonyl oxygen atoms, of which one branch is intramolecular and the other intermolecular. The latter intermolecular branches form a hydrogen-bonded dimer. These characteristic hydrogen bonds seem to play a role in increasing the contribution from the dipolar ionic forms to the ground state of the tropolone molecule.

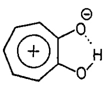
Introduction

Tropolone (I) is a representative of the non-benzenoid aromatic compounds. It is of special interest in connexion with the well-known Hückel $(4n+2)\pi$ rule of aromaticity. Many organic and physicochemical studies have been carried out and a new branch of chemistry, called troponoid chemistry, has been developed (Nozoe, 1959).

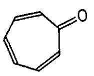
At an earlier stage of investigation, the chemical stability of tropolone in contrast to tropone (II) was attributed to a fairly large contribution from the dipolar resonance form (I*a*) (Nozoe, Seto & Ikemi, 1951; Kubo, Kurita & Kimura, 1954). The crystal structure analyses of tropolone hydrochloride and sodium tropolonate have proved that the delocalized 6π- and 10π-electron systems (III and IV) prevail in the cation and anion of tropolone respectively (Sasada, Osaki & Nitta, 1954; Sasada & Nitta, 1956, 1957; Shiono, 1961).



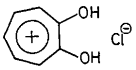
(I)



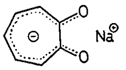
(I*a*)



(II)



(III)



(IV)

On the other hand, it has been recently claimed that the dipolar character of tropolone itself has been overestimated and that the ground state of this system is adequately described as polyolefinic (Bertelli, Andrews & Crews, 1969).

Therefore, it became desirable to determine a detailed molecular structure of tropolone. The electron diffraction study was reported, but the planarity of the ring and the equal C–C lengths were assumed (Kimura & Kubo, 1953).

As for X-ray analysis, only unpublished two-dimensional work has been available so far (Nitta, Osaki & Matsuda, 1952).

The present study has been undertaken to provide information on the molecular geometry of tropolone. A preliminary report on the structure has already been published (Shimanouchi & Sasada, 1970).

Experimental

Tropolone crystallizes from an aqueous solution in the form of colourless plates elongated along the c axis. The crystals are highly volatile. The unit-cell dimensions were determined from the Weissenberg photographs about the three principal axes taken with Cu $K\alpha$ radiation and refined by the least-squares method with the spacings of ten $0kl$, twenty $h0l$ and twelve $hk0$ reflexions at high angles, calibrated with those of the superimposed Al powder lines.

The crystal data are: Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), $C_7H_6O_2$, M.W. 122·1, m.p. 50–51 °C. Monoclinic, $a=7{\cdot}135\pm0{\cdot}004$, $b=12{\cdot}178\pm0{\cdot}005$, $c=7{\cdot}122\pm0{\cdot}007$ Å, $\beta=99{\cdot}63\pm0{\cdot}05°$. Absent spectra, $0k0$ when k is odd and $h0l$ when l is odd. Space group, $P2_1/c$. $U=610{\cdot}1$ Å^3. $D_x=1{\cdot}329$ g cm^{-3}, $Z=4$. Since the substance is fairly soluble in water and various kinds of organic solvent, accurate measurement of the density was very difficult and not carried out in the present investigation. Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu=8{\cdot}24$ cm^{-1}.

The intensity data were collected from equi-inclination Weissenberg photographs at 21 ± 1 °C for the layer lines from 0 to 5 about the a and the c axes, using Cu $K\alpha$ radiation. The crystals were enclosed in 0·7 mm diameter thin-walled Lindemann-glass capillaries to minimize loss by sublimation. The cross sections of the crystals used, perpendicular to the rotation axes, were $0{\cdot}05\times0{\cdot}02$ cm for the a axis and $0{\cdot}04\times0{\cdot}015$ cm for the c axis.

The intensities were estimated visually for the preliminary structure analysis. Since, however, a TV densitometer became available (Izumi, 1971), which provided a more accurate and timesaving method (Shimanouchi, Ibata & Sasada, 1972), the intensities were remeasured by the TV densitometer for the present report. The multiple-film technique was used; the range in relative intensities was 36000 to 1. Out of 1215 independent reflexions recorded (about 81·2% within the Cu sphere), 359 were too weak to be measured. The corrections for the Lorentz and polarization factors were made as usual and those for the spot-size variation in the higher-layer photographs by the method of Takenaka (1972*b*). The correction for absorption was omitted.

The data were put on an absolute scale by the use of a Wilson plot. The normalized structure factor magnitudes, $|E_h|$, were also evaluated; the statistical averages were 0·722 for $|E|$, 0·992 for $|E^2-1|$ and 0·981 for $|E^2|$, $|E|$ values for the unobserved reflexions being assigned to zero.

Structure determination

The structure was determined by the symbolic addition method (Karle & Karle, 1966), using the program *SORTE* (Nakatsu, 1967). After failure to give an interpretable E map from the two different starting sets of phases, the third choice of the starting set, shown in Table 1, led to a reasonable structure. The 160 reflexions with $|E| \geq 1{\cdot}5$ were used in the sign-determining procedure using the $\sum_2$ relationship. Signs were accepted when the probability was 0·998 or higher at the initial stage. After 4 cycles of procedure, 122 signs including symbols were determined, the lower limit of the probability being decreased stepwise down to 0·97. There was much indication in the final $\sum_2$ list that $a=b=-1$ and $c=+1$. An E map computed with these 122 reflexions (about fourteen per atom) showed clearly the positions of the nine non-hydrogen atoms in the asymmetric unit. The relative peak heights assigned to atoms ranged from 236 to 408, while the maximum of the spurious peaks was 192. Of the 122 phases, only one was later found to be incorrect.

Table 1. *Starting set for the application of* $\sum_2$

h	k	l	$\vert E\vert$	Sign
1	1	−6	2·69	+
3	10	−5	3·42	+
1	11	5	2·78	+
2	10	−3	2·57	*a*
5	5	4	2·76	*b*
4	8	−3	3·30	*c*

The atomic coordinates and isotropic temperature factors thus obtained were refined by the block-diagonal matrix least-squares method. After three cycles of the refinement, the discrepancy value, $R=\sum||F_o|-|F_c||/\sum|F_o|$, was reduced to 0·216 for the observed reflexions. The subsequent refinements were performed by introducing anisotropic temperature factors for all the non-hydrogen atoms. After six cycles, the R value was 0·110. At this stage, the three strongest reflexions seemed to be affected by secondary extinction from large discrepancies between $|F_o|$ and $|F_c|$. On the difference electron density map synthesized without these reflexions, all the hydrogen atoms were located unambiguously. The hydrogen atoms were included in further least-squares refinements; the positions and isotropic temperature factors of the hydrogen atoms were allowed to shift. After five cycles no significant changes in parameters were observed and the R value reached 0·054 for the observed reflexions, excluding the three strongest reflexions. When these were included, $R=0{\cdot}060$. A weighting scheme was: $w=1$ for the observed reflexions (except for the three strongest reflexions) and $w=0$ for the unobserved ones. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and the temperature factors are given in Table 2, and their standard deviations in Table 3. The observed and calculated structure factors are listed in Table 4.

Table 2. *Final atomic coordinates and temperature factors*

The anisotropic temperature factors are expressed in the form

$$\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\times 10^{-6}\}.$$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	0·2907	0·4617	0·9412	25128	6279	52659	−1824	4407	2681
O(2)	0·5695	0·3279	1·0040	22256	8409	62418	1576	4587	1590
C(1)	0·2420	0·3622	0·9258	23673	6658	28054	−338	7020	1953
C(2)	0·3972	0·2834	0·9579	22489	7662	34580	1364	6164	2195
C(3)	0·3892	0·1704	0·9483	32555	7178	42528	5178	7748	1849
C(4)	0·2318	0·1019	0·9029	40267	6458	36543	−17	13342	−53
C(5)	0·0468	0·1270	0·8575	37572	7686	31263	−8081	12436	−2602
C(6)	−0·0368	0·2322	0·8509	26280	10043	30061	−6020	6875	−924
C(7)	0·0482	0·3331	0·8827	22974	7661	30615	−724	6437	983

Table 2 (*cont.*)

	x/a	y/b	z/c	B(Å^2)
H(2)	0·554	0·404	0·995	6·3
H(3)	0·526	0·128	0·978	4·4
H(4)	0·265	0·019	0·900	5·3
H(5)	−0·052	0·061	0·818	4·8
H(6)	−0·190	0·234	0·820	4·6
H(7)	−0·051	0·402	0·875	4·7

Table 3. *Estimated standard deviations*

$\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2.

For the non-hydrogen atoms $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ are multiplied by 10^4, $\sigma(B_{ij})$ by 10^6.

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
O(1)	16	15	21	400	116	624	352	779	445
O(2)	16	17	23	391	141	754	388	864	527
C(1)	22	21	24	526	159	592	472	876	519
C(2)	22	23	26	518	179	681	498	940	598
C(3)	26	24	30	706	186	849	585	1230	665
C(4)	28	23	28	795	181	777	609	1281	606
C(5)	28	24	27	755	193	681	616	1158	597
C(6)	24	26	26	579	216	653	596	966	630
C(7)	22	23	25	531	178	642	503	917	548

Table 3 (*cont.*)

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
H(2)	0·026	0·026	0·027	0·7
H(3)	0·023	0·023	0·024	0·6
H(4)	0·024	0·025	0·025	0·7
H(5)	0·023	0·024	0·025	0·6
H(6)	0·022	0·024	0·024	0·6
H(7)	0·023	0·024	0·025	0·6

Thermal motion

The thermal ellipsoids of atoms are shown in Fig. 1(*a*). It is evident that the hydrogen-bonded dimer unit undergoes a rigid-body rotational motion around the centre of symmetry at $\frac{1}{2},\frac{1}{2},0$. Then the thermal motion of the molecular pair has been analysed in terms of the tensors of translation $\mathbf{T}$ and libration $\boldsymbol{\omega}$, assuming that a rigid body consists of the entire 18 atoms (Cruickshank, 1956). A negative ω_{22} value was obtained and the agreement between observed and calculated U_{ij}'s was not good, especially for U_{33}'s. The discrepancy may be due to the internal molecular vibration, the out-of-plane bending of the two C–O bonds, which is seen in Fig. 1(*b*). Therefore, the analysis was performed by giving a zero weight to the oxygen atoms. The results are shown in Table 5. The largest discrepancy between the observed and calculated U_{ii} is about 14·6% for U_{11} of C(3), but the average discrepancy is 5·2%, excluding the O(1) and O(2).

The rigid-body vibration of the hydrogen-bonded dimer has already been reported for the crystal of picolinamide (Takano, Sasada & Kakudo, 1966). This feature of thermal motion of the present molecule is consistent with the molecular packing in the crystal as will be mentioned later.

In order to correct the bond lengths and angles for libration, the eigenvalues of $\boldsymbol{\omega}$ were computed, but because of experimental errors or internal vibration, one of them took a small negative value ($-0·20$ deg^2). In the calculation of the corrected bond lengths, this value was replaced by zero, and for the two C–O bonds the effect of riding motion was also taken into account.

The computations were done on a HITAC 5020E computer in the University of Tokyo and on a HITAC 8500 computer in Tokyo Institute of Technology. The programs in the Universal Crystallographic Computation Program System (1967) were used with some modifications. The programs, *TDRW* for data reduction (Takenaka, 1972*b*) and *DEAM* for plotting of the thermal ellipsoid (Takenaka, 1972*a*) were also used.

Table 4. *Observed and calculated structure factors* (×9)

An asterisk following *k* signifies the reflexion is excluded in the final least-squares refinement because of secondary extinction.

Table 5. *Rigid-body thermal analysis of the seven-membered ring pair*

$$\mathbf{T}=\begin{pmatrix}0{\cdot}0578 & 0{\cdot}0064 & 0{\cdot}0022\\ & 0{\cdot}0402 & -0{\cdot}0039\\ & & 0{\cdot}0734\end{pmatrix}\ \text{Å}^2 \qquad \omega=\begin{pmatrix}23{\cdot}27 & 3{\cdot}46 & 0{\cdot}30\\ & 0{\cdot}33 & -0{\cdot}30\\ & & 5{\cdot}93\end{pmatrix}\ \text{deg}^2$$

$$\sigma(\mathbf{T})=\begin{pmatrix}0{\cdot}0015 & 0{\cdot}0015 & 0{\cdot}0015\\ & 0{\cdot}0028 & 0{\cdot}0028\\ & & 0{\cdot}0040\end{pmatrix} \qquad \sigma(\omega)=\begin{pmatrix}5{\cdot}42 & 0{\cdot}53 & 1{\cdot}03\\ & 0{\cdot}53 & 0{\cdot}47\\ & & 0{\cdot}47\end{pmatrix}$$

Observed and calculated U_{ij}'s in Å²

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	obs.	0·049	0·062	0·135	0·006	0·009	−0·006
	calc.	0·059	0·043	0·078	0·004	0·002	−0·004
O(2)	obs.	0·065	0·055	0·160	−0·002	0·008	−0·001
	calc.	0·062	0·044	0·096	0·011	0·002	−0·004
C(1)	obs.	0·053	0·057	0·070	0·004	0·004	−0·003
	calc.	0·058	0·051	0·073	0·004	0·002	−0·003
C(2)	obs.	0·061	0·054	0·087	0·000	0·005	−0·003
	calc.	0·059	0·053	0·084	0·011	0·002	−0·004
C(3)	obs.	0·073	0·062	0·109	0·017	0·002	−0·005
	calc.	0·062	0·066	0·105	0·017	0·003	−0·003
C(4)	obs.	0·065	0·085	0·091	0·024	0·001	−0·002
	calc.	0·060	0·087	0·097	0·017	0·003	−0·002
C(5)	obs.	0·053	0·099	0·078	0·010	−0·001	−0·000
	calc.	0·058	0·096	0·075	0·005	0·002	−0·001
C(6)	obs.	0·060	0·081	0·076	−0·010	0·000	−0·002
	calc.	0·061	0·082	0·075	−0·005	0·002	−0·001
C(7)	obs.	0·056	0·059	0·077	−0·001	0·003	−0·002
	calc.	0·062	0·062	0·080	−0·003	0·002	−0·002

These are all referred to the inertial axes of the two seven-membered rings designated by *A* and *B* in Fig. 5, the centre of gravity being ½, ½, 1.

The inertial axes and their direction cosines, *l*, *m*, *n*, to the crystal axes, *a*, *b*, *c*, are as follows:

Axis	*l*	*m*	*n*
1	0·5602	0·8298	0·1733
2	0·8426	−0·5559	0·1709
3	−0·0701	−0·0496	0·9847

Table 6. *Intermolecular non-bonded contact distances*

The C···C and C···O distances shorter than 3·7 Å and those involving the hydrogen atom shorter than 3·0 Å are listed.

Atom in (*A*)	Distance (Å)
C(2)···C(2) (*C*)	3·653
C(2)···C(3) (*C*)	3·663
C(3)···O(2) (*C*)	3·610
C(3)···C(2) (*C*)	3·548
C(4)···O(1) (*C*)	3·471
C(4)···C(1) (*C*)	3·439
C(5)···C(1) (*C*)	3·584
C(5)···C(7) (*C*)	3·418
C(6)···C(6) (*C*)	3·587
C(6)···C(7) (*C*)	3·578
H(4)···H(5) (*D*)	2·89
H(5)···H(5) (*D*)	2·98
O(2)···C(6) (*E*)	3·385
O(2)···C(7) (*E*)	3·661
O(2)···H(6) (*E*)	2·60
H(3)···H(6) (*E*)	2·80
O(1)···C(5) (*F*)	3·558
O(1)···H(5) (*F*)	2·59
H(7)···H(4) (*F*)	2·68
H(7)···H(5) (*F*)	2·56
O(1)···H(7) (*G*)	2·86
H(3)···H(4) (*H*)	2·39

Table 6 (*cont.*)

Symmetry code*:

(*A*)	x,	y,	z
(*B*)	$1-x$,	$1-y$,	$2-z$
(*C*)	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
(*D*)	$1-x$,	$\frac{1}{2}+y$,	$1\frac{1}{2}-z$
(*E*)	$1+x$,	y,	z
(*F*)	$\bar{x}$,	$\frac{1}{2}+y$,	$1\frac{1}{2}-z$
(*G*)	$\bar{x}$,	$1-y$,	$2-z$
(*H*)	$1-x$,	$\bar{y}$,	$2-z$

* These are also indicated in Figs. 2 and 5.

Results and discussion

Crystal structure

The packing diagram of the crystal viewed along the *a* axis is shown in Fig. 2. Two molecules, related to each other by centre of symmetry at ½,½,0, form a hydrogen-bonded dimer as described later in detail. The intermolecular distances between the hydrogen-bonded dimers are all longer than the sum of the van der Waals radii as shown in Table 6. The weak van der Waals interaction is consistent with the highly volatile property of this crystal. All the molecular planes are nearly perpendicular to the (010) plane with the di-

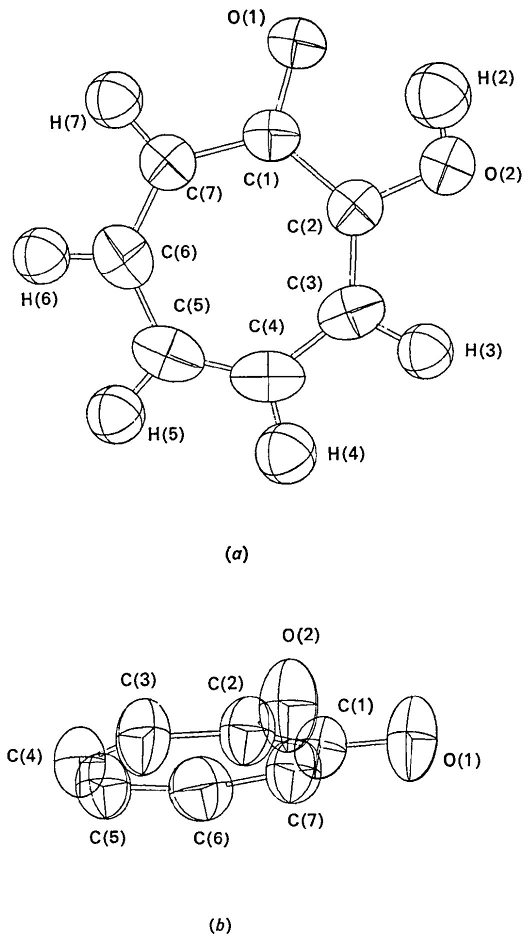


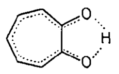
Fig. 1. Thermal ellipsoids at the 50% probability level, (*a*) viewed along the *c* axis, (*b*) viewed along the *a* axis, the hydrogen atoms being omitted for clarity.

hedral angle of 92·6° and nearly parallel to the $(10\bar{4})$ plane with the angle of 2·6°.

Molecular geometry

The bond lengths and angles are illustrated in Fig. 3 and the former, corrected for thermal motion, are listed in Table 7. Since these corrections are fairly small, the following discussion is based on the uncorrected values. The corrected bond angles are not given; the corrections are not greater than 0·2°.

It has been proposed that the oxygen atoms are equivalent and the hydroxyl hydrogen is symmetrically situated with respect to the two oxygen atoms as in (I*b*) (Dewar, 1945; Nozoe, 1949; Erdtman & Gripenberg, 1948).



(I*b*)

Table 7. *Bond lengths* (Å)

Bond	Uncorrected*	Corrected	Predicted‡
C(1)–C(2)	1·454 (4)	1·460	1·462
C(2)–C(3)	1·379 (4)	1·381	1·355
C(3)–C(4)	1·393 (4)	1·393	1·452
C(4)–C(5)	1·341 (4)	1·344	1·357
C(5)–C(6)	1·410 (4)	1·415	1·452
C(6)–C(7)	1·373 (4)	1·374	1·355
C(1)–C(7)	1·410 (3)	1·412	1·462
C(1)–O(1)	1·261 (3)	1·266†	1·258
C(2)–O(2)	1·333 (3)	1·339†	1·389
O(2)–H(2)	0·94 (3)		
C(3)–H(3)	1·09 (2)		
C(4)–H(4)	1·04 (3)		
C(5)–H(5)	1·07 (3)		
C(6)–H(6)	1·08 (3)		
C(7)–H(7)	1·09 (3)		

* The e.s.d.'s given in parentheses refer to the last significant digits.

† With the correction for riding motion of the oxygen atoms combined with the rigid-body correction.

‡ Dewar & Trinajstić (1970).

However, this view can be excluded by the difference synthesis; there is a definite peak corresponding to the hydrogen atom attached to O(2) and no significant feature around O(1). In addition, the C(1)–O(1) distance, 1·261 Å, is significantly shorter than the C(2)–

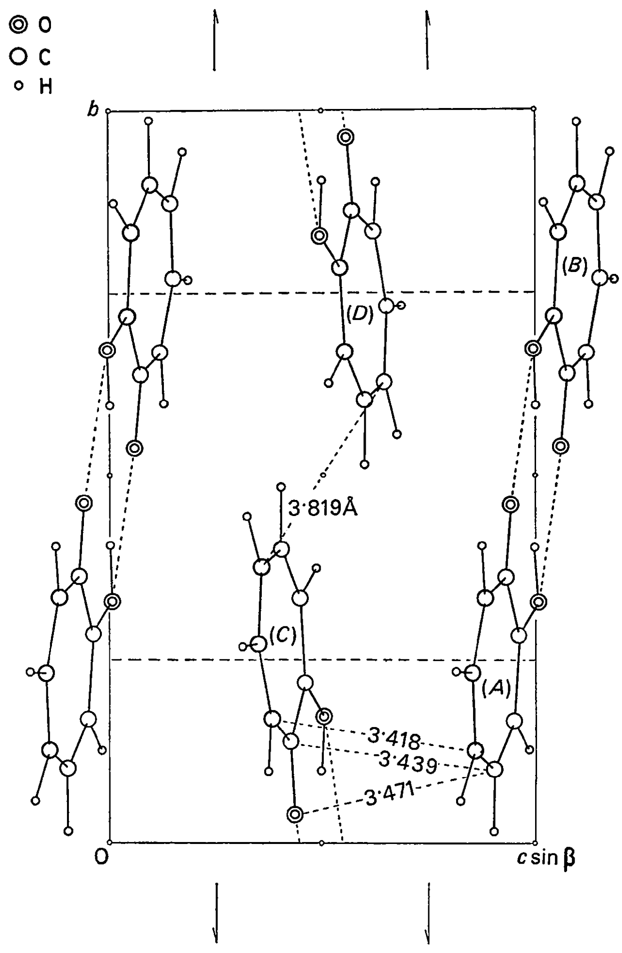
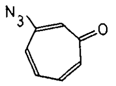


Fig. 2. Crystal structure viewed along the *a* axis. Some intermolecular distances are shown.

O(2), 1·333 Å, consistent with exclusive bonding of H(2) to O(2).

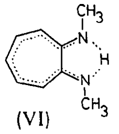
Although it seems that bond alternation is observed in the seven-membered ring, its degree is remarkably reduced in comparison with that of 3-azidotropone (V) (Cruickshank, Filippini & Mills, 1972).



(V)

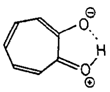
That is, the formal double bonds, C(2)–C(3) and C(6)–C(7), are significantly longer than the corresponding bonds in (V) and the formal single bonds are nearly equal to the typical aromatic value except for C(1)–C(2). The C(4)–C(5) bond is significantly shorter than the others and is as short as the corresponding one in (V). The averaging effect of the bond lengths may not be exerted upon the distant part of the seven-membered ring from the electron-attracting carbonyl group.

The C(1)–C(2) length, 1·454 Å, is significantly longer than the others. It is interesting to compare this bond length with the corresponding ones in the related compounds as shown in Table 8. In the 10π-electron systems of *N*,*N*′-dimethylaminotroponeimine (VI) (Goldstein & Trueblood, 1967)



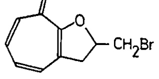
(VI)

and sodium tropolonate (IV) (Sasada & Nitta, 1956; Shiono, 1961), the bond lengths are found to be 1·490 Å, which is in good agreement with that expected for a single bond between trigonally hybridized carbon atoms (Ammon & Sundaralingam, 1966). On the other hand, in tropolone hydrochloride (III) (Sasada & Nitta, 1957), where a delocalized 6π-electron system prevails, the corresponding length is 1·396 Å. The distance in the present molecule lies between the two types. This feature of the seven-membered ring geometry is also consistent with the carbon–oxygen lengths. As shown in Table 8, the observed C(1)–O(1) distance is much longer than that in (V), and the C(2)–O(2) length is comparable to that in (III). These features seem to be reasonably explained by assuming the three main canonical formulae (I, I*a* and I*c*) contribute to the structure.



(I*c*)

Comparison of the C(7)–C(1)–C(2) angles of the seven-membered ring may also suggest the significant contribution from the dipolar ionic structure. It has been reported that the C–CO–C angle has some correlation to the C=O length (Schleyer & Nicholas, 1961). Therefore, this angle can be used as a measure of polarization of the carbonyl group. The corresponding angles in (VII) (Shimanouchi, Ashida, Sasada, Kakudo Murata & Kitahara, 1967)



(VII)

and tropolonyl *p*-chlorobenzoate (Schaefer & Reed, 1971) in which the contribution from a dipolar ionic form is small are 121·5 and 120·3° respectively. The angle, 124·2°, in tropolone is larger than the above values, compatible with the significant carbonyl polarization.

Another measure of the contribution from (I*a*) is a planarity of the molecule. The perpendicular displacements of atoms from some least-squares planes are given in Table 9. The deviations of the seven ring atoms and the O(2) atom are small, amounting to no more

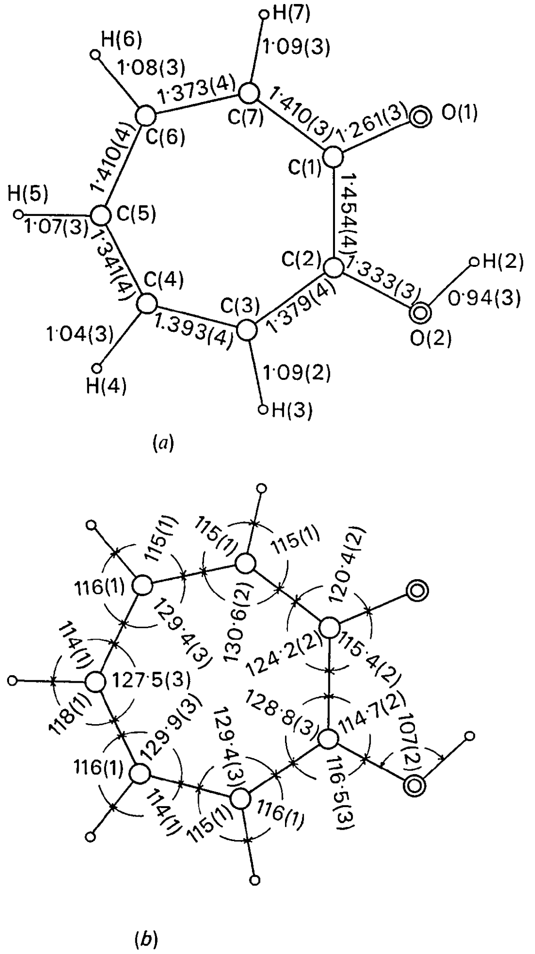


Fig. 3. (*a*) Bond lengths (Å) (*b*) Bond angles (°) The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions.

Table 8. *Comparison of* C(1)–C(2) *and* C–O *distances* (Å)

Compound	3-Azidotropone(a)	*N,N'*-Dimethylaminotroponeimine(b)	Sodium tropolonate(c)	Tropolone(d)	Tropolone hydrochloride(e)
C(1)–C(2)		1·490	1·490	1·454	1·396
C–O	1·234		1·284	1·261 (C=O)	1·318
				1·333 (C–O)	1·321

The C=O lengths in various quinones are 1·214~1·224 and typical C(sp^2)–O single bond lengths are 1·343~1·358 Å (Hall & Nobbs, 1966).

References: (*a*) Cruickshank, Filippini & Mills (1972)
(*b*) Goldstein & Trueblood (1967)
(*c*) Sasada & Nitta (1956), Shiono (1961)
(*d*) Present work
(*e*) These values are obtained from the least-squares refinement with the three-dimensional reflexion data of Sasada & Nitta (1957).

Table 9. *Some least-squares planes*

Plane	I	II	III	IV	V	VI
l	0·2385	0·2373	0·2202	0·2350	0·2464	0·2181
m	0·0449	0·0534	0·0223	0·0523	0·0689	0·0139
n	−0·9701	−0·9700	−0·9752	−0·9706	−0·9667	−0·9758
p	5·964	5·942	6·108	5·959	5·892	6·146
			Deviations of atoms (Å)			
O(1)	0·032*	0·058	−0·002*	0·063	0·126	−0·017
O(2)	−0·012*	−0·002	−0·047	−0·000	0·059	−0·052
C(1)	0·004*	0·020*	0·004*	0·028	0·066	0·000*
C(2)	−0·003*	0·004*	−0·001*	0·010*	0·045	0·000*
C(3)	−0·010*	−0·015*	0·023	−0·008*	0·004*	0·036
C(4)	0·007*	−0·004*	0·080	0·007	−0·009*	0·103
C(5)	0·028*	0·021*	0·119	0·035	0·008*	0·142
C(6)	−0·010*	−0·005*	0·063	0·008*	−0·004*	0·076
C(7)	−0·036*	−0·021*	−0·002*	−0·010*	0·006	0·000*
H(2)	0·06	0·08	0·01	0·08	0·16	−0·00
H(3)	−0·01	−0·02	0·01	−0·02	−0·00	0·03
H(4)	0·04	0·02	0·13	0·03	0·00	0·16
H(5)	0·11	0·09	0·23	0·11	0·06	0·26
H(6)	−0·05	−0·04	0·04	−0·03	−0·05	0·06
H(7)	−0·11	−0·09	−0·08	−0·08	−0·06	−0·09

The equations of the planes are expressed in the form

$$lx'+my'+nz'+p=0, \text{ where } x'=x+z\cos\beta,\ y'=y \text{ and } z'=z\sin\beta .$$

* Distances with asterisks refer to atoms defining the plane.

Interplanar angles in degrees between the planes

Plane	I	II	III	IV	V	VI
I	—	0·5	1·7	0·5	1·5	2·2
II		—	2·1	0·2	1·1	2·5
III			—	1·9	3·1	0·5
IV				—	1·2	2·4
V					—	3·6

than 0·021 Å. Furthermore the hydroxyl hydrogen atom, H(2), also lies in the molecular plane.

From our systematic analyses of various benzotropones, it has been revealed that the tropone nuclei take more or less a boat form. In order to define the shape of a boat, it is convenient to use the angles, δ_1, δ_2 and δ_3, as shown in Fig. 4. These values for several tropone derivatives are listed in Table 10. It is clearly shown that tropolone is more planar than any benzotropones.

The average intramolecular distance between the hydrogen atoms on adjacent carbon atoms of the ring is 2·30 Å, similar to that in (VI). This distance is shorter than the corresponding one in benzene because of the increased internal angles, but is not short enough to exert strong repulsion.

Table 10. *Comparison of planarity of seven-membered rings*

	Angles (°)*			
Compound	δ_1	δ_2	δ_3	Reference
Dibenzo[*b,f*]tropone	36·9	20·0	5·7	(1)
2,7-Dimethyl-4,5-benzotropone	11·5	4·7	2·5	(2)
5-Chloro-2,3-benzotropone	11·7	2·8	2·7	(3)
5,7-Dibromo-2,3-benzotropone	5·9	1·2	0·7	(3)
4,5-Benzotropone	3·6	3·7	−2·0	(4)
Tropolone	2·4	1·2	0·8	(5)

References

(1) Shimanouchi, Hata & Sasada (1968)
(2) Ibata, Shimanouchi & Sasada (1972*b*)
(3) Ibata, Shimanouchi & Sasada (1972*a*)
(4) Hata, Shimanouchi & Sasada (1969)
(5) Present work

* See Fig. 4.

Dimer formation in the crystal

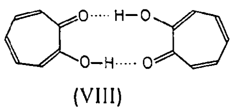
As shown in Fig. 5, the molecules related to each other by the centre of symmetry form a hydrogen-bonded dimer. Since the centre lies only 0·020 Å above the seven-membered ring plane of the molecule, the two molecules are practically coplanar. In the centrosymmetric hydrogen-bonded dimers of organic acids, the perpendicular separation between the parallel carboxyl groups varies from zero (coplanar) to 0·5 Å (Robertson, 1964; Jeffrey & Sax, 1963). The good coplanarity of the dimer in the present crystal may imply that the hydrogen bonding force prevails in the molecular packing.

Details of the molecular association are given in Fig. 5. Both of the O(1)···H(2) and O(1)···H(2) (*B*) distances are 1·98 Å. The O(2)–H(2)–O(1) (*B*) angle is 138° and the O(2)–H(2)–O(1) is 118°. These values lie within the range of possible hydrogen bonding. It is, therefore, indicated that the hydrogen atom H(2) joins not only to O(1) (*B*) but also to O(1), and hence participates in a bifurcated hydrogen bond.

A characteristic diamond-shape arrangement of O(1), O(2), O(1) (*B*) and O(2) (*B*), as shown in Fig. 6(*a*), seems to be favourable to the bifurcated hydrogen bond. If two lone pairs of the carbonyl oxygen atom O(1) are assumed to extend at 120° to the C(1)–O(1) bond and are coplanar with the C(2)–O(2) bond, one of the lone pairs points to the centre of the dimer and overlaps, to the same extent, with the two hydrogen atoms, H(2) and H(2) (*B*). Thus H(2) participates, most effectively, in the bifurcated hydrogen bond, one branch being intramolecular and the other intermolecular. The O(1)–C(1)–C(2) angle is definitely smaller than the O(1)–C(1)–C(7). This may be due to the intramolecular branch of the hydrogen bond.

It is noted that the assumed lobes of the lone pairs are nearly on a straight line with the head-to-head contact as shown in Fig. 6(*a*). The distance, O(1)···O(1) (*B*), is 3·108 Å. On the other hand, the unusually short non-bonded O···O distance, 2·553 Å, is reported in myxin (Hanson, 1968). In this case, the lobes of the lone pairs are directed so as to avoid the head-to-head interaction, as shown in Fig. 6(*b*). A similar situation has also been reported in iodinine (Hanson & Huml, 1969) and 1,5-dihydroxyanthraquinone (Hall & Nobbs, 1966). Thus, these contact distances may provide information about the steric distribution of the lone pair electrons in the oxygen atoms of this type.

From the infrared spectroscopic study, the hydrogen-bonded dimer structure (VIII) has been assumed in the solid state of tropolone (Kuratani, Tsuboi & Shimanouchi, 1952). As the present work has revealed more complicated features, however, further explanation for some complex pattern in the OH stretching might be possible in terms of the bifurcated hydrogen bond.



(VIII)

This specific feature of hydrogen bonding seems to play an important role in stabilization of the tropolone molecules, described in the previous paragraph. The two hydrogen bondings to the carbonyl oxygen, O(1), may enhance the polarization $>\overset{+}{C}-\overset{-}{O}$, and hence increase the contribution from the resonance form (I*a*) with aromatic sextet in the seven-membered ring nucleus. It has been reported that even one hydrogen

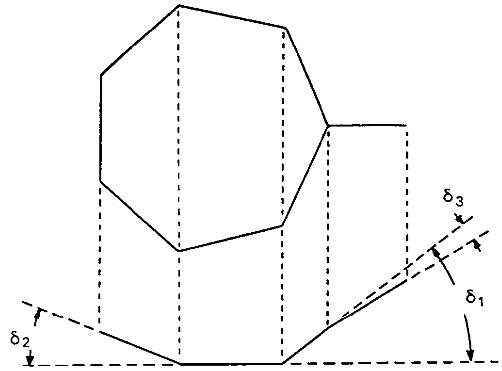


Fig. 4. The boat shape of the molecule, defining angles δ_1, δ_2 and δ_3.

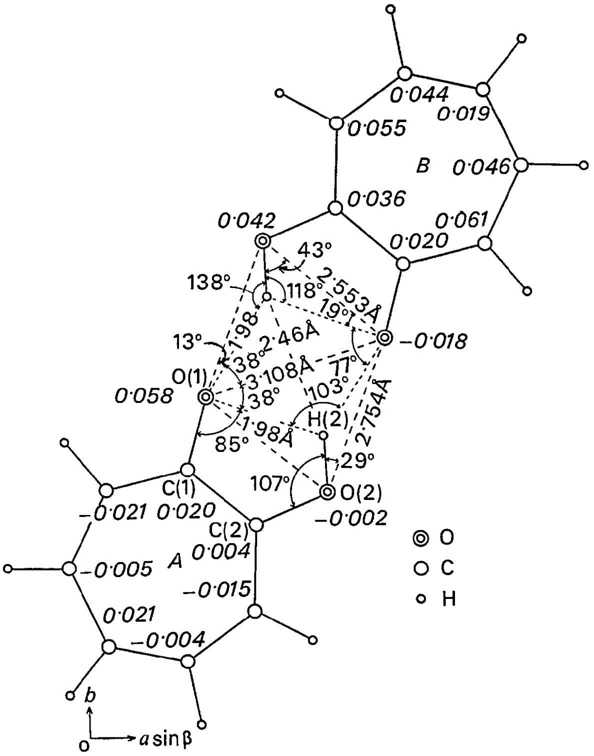


Fig. 5. Details of hydrogen bonding. Italic type indicates the deviations (Å) of atoms from the least-squares plane II in Table 9.

bond has such an effect on the oxygen atom (Hanson, 1968). Conversely, in the compound (VII) (Shimanouchi, Ashida, Sasada, Kakudo, Murata & Kitahara, 1967) and tropolonyl *p*-chlorobenzoate (Schaefer & Reed, 1971) which do not contain any hydrogen bonding groups, the seven-membered rings have definite bond alternation and the dipolar form has little contribution.

Aromaticity of tropolone

As previously mentioned, there have been some controversies on the aromaticity of tropolone. Recently, Dewar & Trinajstić (1970) have concluded by a semi-empirical SCF MO method that tropolone is not aromatic. However, the agreement between the bond lengths predicted by them and those observed is not good, as shown in Table 7.

Hosoya, Tanaka & Nagakura (1962) have reported that the ultraviolet spectrum of tropolone crystals can be interpreted as that of a hydroxyl derivative of tropone. Since their assignment of the carbonyl and the hydroxyl oxygen atoms in the crystal has been proved to be the reverse of that indicated in the present analysis, however, it may be necessary to re-examine the result of the spectral work.

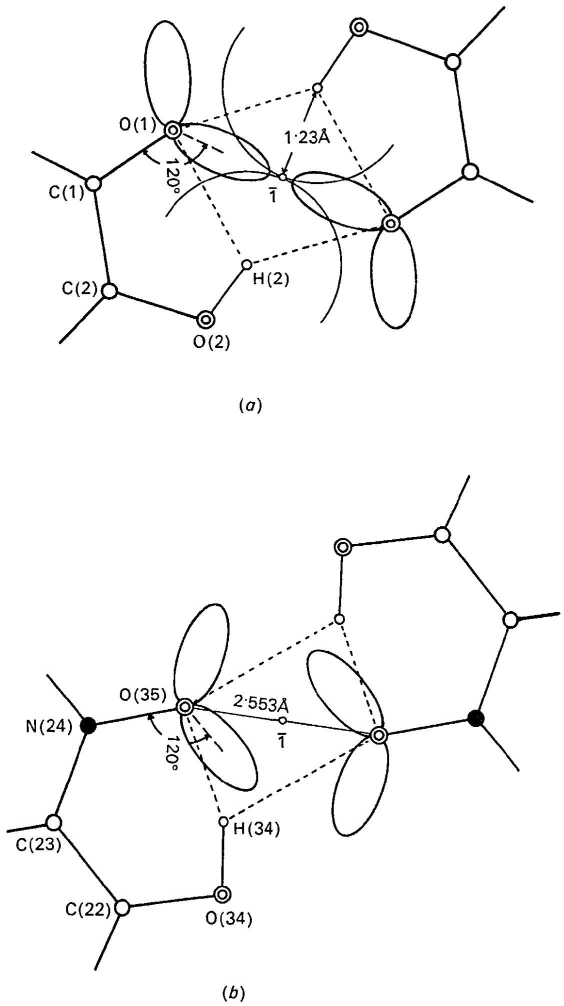


Fig. 6. Arrangement of oxygen atoms with respect to 1̄. (*a*) Tropolone. (*b*) Myxin.

From the structural evidence of the detailed molecular geometry revealed by the present crystal structure analysis, it may be concluded that in the crystalline state tropolone is not merely a 2-hydroxy derivative of tropone, but has a fairly large aromatic character by significant contribution from the dipolar ionic form (I*a*).

In solution it may be possible that at least one intramolecular hydrogen bond exists; therefore some contribution from (I*a*) can also be assumed to the isolated molecule. This is compatible with the varying chemical behaviour of this compound (Nozoe, 1959).

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Hydrogen Bonding in the Crystalline State. Crystal Structure of $CaHAsO_4.3H_2O$*

By M. Catti and G. Ferraris

Istituto di Mineralogia e Geochimica dell'Università, via S. Massimo 24, 10123 *Torino, Italy*

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Calcium hydrogen arsenate trihydrate ($CaHAsO_4.3H_2O$) crystallizes in the orthorhombic system, space group *Pbca*. Unit-cell parameters are: $a_0 = 11\cdot195$ (1), $b_0 = 10\cdot713$ (2), $c_0 = 11\cdot179$ (2) Å; $Z = 8$. The crystal structure was refined anisotropically to $R = 0\cdot034$, using 1321 non-zero reflexions measured on an automatic three-circle diffractometer (Cu $K\alpha$ radiation). Corrections for absorption, secondary extinction and anomalous scattering were applied. The hydrogen atoms were located from a difference map, and one of the three water molecules appears very weakly hydrogen bonded. $CaHAsO_4.3H_2O$ is isostructural with $MgHPO_4.3H_2O$ (newberyite) and with $MnHPO_4.3H_2O$; its crystal structure is built up from isolated Ca octahedra sandwiched between As tetrahedra. The resulting layers, parallel to (100), are connected by infinite zigzag chains of hydrogen bonds along [100]. Some common features of the related compounds $CaHAsO_4$ (weilite), $CaHAsO_4.H_2O$ (haidingerite), and $CaHAsO_4.2H_2O$ (pharmacolite) are discussed.

Introduction

Calcium hydrogen arsenate trihydrate, $CaHAsO_4.3H_2O$, is the most highly hydrated member of the group including $CaHAsO_4.2H_2O$ (pharmacolite), $CaHAsO_4.H_2O$ (haidingerite) and $CaHAsO_4$ (weilite), which have been studied both by X-ray (Ferraris, 1969; Calleri & Ferraris, 1967; Ferraris & Chiari, 1970) and neutron diffraction (Ferraris, Jones & Yerkess, 1971, 1972) with the aim of characterizing the hydrogen bond in the crystalline state (*cf.* Ferraris & Franchini-Angela, 1972). With the same aim, neutron, diffraction studies of the related compounds $CaHPO_4$, monetite (Denne & Jones, 1971), and $CaHPO_4.2H_2O$, brushite (Curry & Jones, 1971), have been recently carried out. The knowledge of the crystal structure of a series of hydrates is important for the understanding of both the role of the water molecule in the structures and the influence of the cation/oxygen stoichiometric

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