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The Crystal Structure of Hydroxylammonium Perchlorate (NH₃OH⁺ClO₄⁻) at −150°C

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Three crystalline phases of hydroxylammonium perchlorate have been examined by X-ray diffraction. The crystal structure of the most stable phase, which is orthorhombic with space group $P2_1cn$ and cell dimensions $a = 7\cdot52(2), b = 7\cdot14(1), c = 15\cdot99(2)$ Å at 25°C, has been determined at -150°C with data collected by the use of the equi-inclination photographic technique. The final $R = \Sigma \, ||F_o| - |F_c||/ \Sigma \, |F_o| = 0\cdot09$ for 1757 observed reflections. The structure consists of chains of perchlorate ion tetrahedra held together by hydrogen bonding from parallel chains of NH_3OH^+ ions. The NH_3OH^+ ions may be rotating with the N–O vector as axis.

Introduction

Hydroxylammonium perchlorate (HAP) crystallizes as colorless but very hygroscopic needles from a mixture of ethanol and chloroform. When the crystals so obtained (called phase A here) are heated, they crack near 55°C (*i.e.* 54–56°C) but retain their external form. Simultaneously, colors appear under the polarizing microscope in a crystal which previously had been in an extinction position. Differential thermal analysis (DTA) studies (Cziesla, 1966; Crisler, 1966) on phase A crystals show an absorption of heat at about 55°C. The above evidence is consistent with a phase change. The phase change is apparently not immediately reversible, although absorption of heat in the DTA studies reappears after the high temperature phase has either been cooled to liquid nitrogen temperatures or has been allowed to stand for about a week.

As part of the elucidation of this phase change and as part of a study of the physical and chemical properties of HAP, the crystal structure at −150°C of the room temperature form (phase A) has been determined and crystals of the high temperature form (phase B,

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melting at about 89–91°C) were examined at 70°C. A third phase (phase C) which melts at about 58°C at atmospheric pressure, presumably the phase the possible existence of which was suggested earlier in order to explain anomalous DTA results (Cziesla, 1966), has been grown in capillaries and examined by single-crystal X-ray diffraction.

Since phase A undergoes the phase transition near 55°C and the closely related phases B and C melt near 90°C and near 58°C respectively, and since disorder or rotation has been reported in perchlorate groups (Gomes de Mesquita, MacGillavry & Eriks, 1965; Karle & Karle, 1966; Sundaralingam & Jensen, 1966) and NH_4^+ groups (Smith & Levy, 1962), the X-ray data on phase A were collected at about −150°C with a Weissenberg camera which had been modified slightly (Dickens, 1966) for routine low temperature work.

Determination of the structure

Roughly cylindrical needle-like crystals of phase A, not more than 0·35 mm in cross-section ($\mu_{Mo} = 8\cdot5$ cm⁻¹) were examined under a microscope attached to a dry box (Crisler, 1964) and were sealed into capillaries. The crystals were found to be orthorhombic, with the cell dimensions in Table 1 and space group $P2_1cn$ or $Pmcn$. Space group $P2_1cn$ ($x, y, z; \frac{1}{2} + x, \bar{y}, \bar{z};$

$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z$) was indicated in the Patterson map, where the centrosymmetric peaks $2x$, $2y$, $2z$ were missing. The choice was substantiated by the eventual refinement of a chemically reasonable structure in $P2_1cn$. The unit cell, therefore, has two formula weights in the asymmetric unit. The observed density is 2·02 and the calculated density is 2·13 g. cm^{-3} at 25 °C.

1757 intensity data taken with Mo radiation on $0 \rightarrow 8kl$ a-axis equi-inclination photographs (a is the needle axis) were estimated visually and corrected for the combined spot extension and Lp effects, but not for absorption. Preliminary estimates of the scale factors for the various equi-inclination levels were obtained in the calculation of quasi-normalized structure factors (Dickinson, Stewart & Holden, 1966).

The form factors for atoms other than hydrogen were taken from *International Tables for X-ray Crystallography* (1962), and those of hydrogen were taken from McWeeny (1951). All form factors used were for isolated neutral atoms.

The structure was solved from the sharpened Patterson function, calculated from the E^2-1 coefficients, and from subsequent F_o Fourier syntheses. It was refined by full-matrix least-squares procedures. The nitrogen atoms were identified by their higher temperature factors ($B_N = 1·5$, $B_O = 0·85$) when they were introduced into the refinement as oxygen atoms. In these refinements the weights for the reflections were calculated from 10/[maximum of ($F_o/2 + 5$) or 10] and the quantity minimized was $\sum_{hkl} w|F_o - F_c|^2$. The x coordinate of the atom Cl(2) was used to define $x = 0$.

The few reflections with $F_c > 60$ at this stage of the refinement apparently suffered from extinction and were, therefore, labeled appropriately and given zero weights in the refinements.

Hydrogen atoms were sought in several difference syntheses, including one at $R = 0·09$, but were not found, presumably in part because of the imprecise phasing present in acentric structure determinations

Table 1. *Cell parameters* of* HAP *phases*

	Phase A		Phase B (at 23 °C)
	25 °C	−150 °C	
a	7·52 ± 0·02 Å	7·46 ± 0·01 Å	7·52 ± 0·03 Å
b	7·14 ± 0·01	7·12 ± 0·01	24·28 ± 0·03
c	15·99 ± 0·02	15·70 ± 0·02	7·13 ± 0·03
z	4		β 95° ± 1°
	8 F. Wts. per cell		z 4
	$P2_1cn$		12 F. Wts. per cell
			$P2_1/n$

	Phase C (at 50 °C)		
	C-centered cell	F-centered cell	Body-centered cell
a	11·67 ± 0·03 Å	16·46 Å	10·21 Å
b	16·34 ± 0·03	16·34	16·34
c	10·00 ± 0·03	11·52	10·03
β	124°35′ ± 1°	90°35′	109°45′
z	4 or 8		
	16 F. Wts. per unit cell		
	$C2/m$, $C2$ or Cm		

* Cell dimensions of phase A determined from Weissenberg and oscillation films and standardized from a superimposed powder pattern of Al taken at room temperature. Other cell dimensions measured from precession films taken with single crystals and not standardized.

Table 2. *Atomic parameters in phase* A *of* HAP

		x	y	z	B
ClO$_4^-$ group	Cl(1)	0·1421 (4)	0·1456 (2)	0·1836 (1)	0·32 (2) Å^2
	O(1)	−0·0093 (11)	0·0123 (7)	0·1861 (3)	0·83 (6)
	O(2)	0·2580 (11)	0·1069 (9)	0·2551 (4)	0·93 (8)
	O(3)	0·0673 (12)	0·3322 (9)	0·1895 (4)	0·99 (8)
	O(4)	0·2405 (11)	0·1213 (9)	0·1059 (4)	1·05 (8)
ClO$_4^-$ group	Cl(2)	0·0000	0·2450 (2)	0·4372 (1)	0·35 (2)
	O(5)	0·1087 (10)	0·0931 (9)	0·4679 (4)	1·05 (8)
	O(6)	0·1141 (10)	0·4011 (8)	0·4144 (3)	0·76 (7)
	O(7)	−0·0993 (12)	0·1811 (10)	0·3646 (4)	1·38 (10)
	O(8)	−0·1229 (11)	0·3025 (8)	0·5043 (3)	0·79 (7)
NH$_3$OH$^+$	N(1)	−0·0104 (12)	0·7893 (8)	0·0282 (3)	0·61 (6)
	O(9)	−0·0032 (11)	0·6509 (7)	0·0927 (3)	0·61 (5)
NH$_3$OH$^+$	N(2)	0·1379 (13)	0·6689 (8)	0·2776 (3)	0·65 (6)
	O(10)	0·1222 (10)	0·7952 (8)	0·3461 (3)	0·73 (6)

x coordinate of Cl(2) used to define origin along **a**.
Average value of shift/error for final cycle = 0·005.
Maximum value of shift/error for final cycle = 0·019.

Table 3. *Observed and calculated structure factors for phase* A

Columns are *l*, 10F_o, 10F_c

Table 3 (cont.)

[Structure factor table — columns of h, k, l groupings with observed and calculated structure factors]

(Olovsson & Templeton, 1959) but possibly also because of oscillation or rotation of the NH_3OH^+ group. A smeared model with half the hydrogen atoms in suitable positions was used to refine the heavier atom parameters to the values reported in Table 2. The observed and calculated structure factors are listed in Table 3.

The largest correlation coefficients are 0·34 between the scale factors and the Cl isotropic temperature factors, 0·25 between the scale factors themselves, 0·21 between the Cl isotropic temperature factors, and 0·1 between the Cl temperature factors and the other temperature factors. All other correlation coefficients are much less than 0·1. The systematically high correlations between the scale factors and the β_{11} (for a axis data) temperature factors prevent the direction of maximum vibrations of individual atoms from being picked out and make anisotropic refinement worthless. Since the crystal was kept at $-150°$ during the data collection the thermal motion should, however, be relatively small.

Discussion of the structure of phase A

The crystal structure of phase A, excluding hydrogen atoms, is shown in Fig. 1. The structure consists of

perchlorate ion tetrahedra in infinite chains along c which are held together by hydrogen bonding from parallel chains of NH_3OH^+ ions. The different chains alternate along **a** and **b**. The closest approach of ClO_4^- tetrahedra, $O(4)-O(8) = 3·03$ Å, is between neighboring groups in the chain along **c**. The NH_3OH^+ ions are arranged with parallel pairs of N–O vectors (Fig. 1) one pair having the N–O vectors roughly 45° and the other −45° to **b**. The ClO_4^- groups present their edges irregularly to six surrounding NH_3OH^+ ions, which are, therefore, arranged in an irregular large octahedron around each ClO_4^- ion. There are seventeen $(N–O)\cdots(ClO_4)$ distances less than the $O(4)\cdots O(8)$ inter-ClO_4^- closest approach.

The intra-ionic distances and angles are given in Table 4 and the inter-ionic distances, which must include those between hydrogen bonded atoms, in Table 5. The Cl–O distances in the ClO_4^- groups [average value $1·45 \pm 0·01$ Å uncorrected for any rotation-oscillation effect (Cruickshank, 1956, 1961] are in good agreement with those of $1·46 \pm 0·01$ Å (NO_2ClO_4, Truter, Cruickshank & Jeffrey, 1960) and $1·462 \pm 0·004$ Å (low temperature form of $H_3O^+ClO_4^-$, Nordman, 1952). The O–Cl–O angles (average value $109·5 \pm 0·04°$) show the ClO_4^- group to be essentially tetrahedral, as expected. The average O–O distance in the ClO_4^- group is $2·36 \pm 0·01$ Å. The average N–O distance of $1·41 \pm 0·01$ Å in the NH_3OH^+ group is near to that expected when the sum $(1·47 \pm 0·02$ Å) of the sp^3 covalent radii (Giguère & Schomaker, 1943) of nitrogen $(0·735$ Å) and oxygen $(0.735$ Å) is corrected (Schomaker &

Stevenson, 1941) by $−0·08 |x_A − x_B| = −0·08 |3·0 − 3·5|$ $= −0·04$ Å to $1·43 \pm 0·02$ Å to account for the difference in the electronegativities of these atoms. In room temperature structure determinations of NH_3OHCl and NH_3OHBr, $1·45$ Å has been found (Jerslev, 1948) for the N–O distance.

The $X–H\cdots Y$ distances for possible hydrogen bonds in phase A are given in Table 5 and the environments of the two NH_3OH^+ groups are shown in Fig. 2 and 3. Since hydrogen can form hydrogen bonds to two or more atoms simultaneously (Baur, 1965) in keeping with the predominantly electrostatic nature (see for example Coulson, 1957) of the hydrogen bond, the $X\cdots Y$ distance is a poor criterion of the strength. However, various $X\cdots Y$ distances for N and O given in Baur (1965) and Coulson (1957) suggest that the hydrogen bonding in phase A is weak. Further, preliminary nuclear magnetic resonance results (Farrar, 1967) indicate that the NH_3OH^+ group in phase A is rotating faster than 10^5 times per second at room temperature. This is substantiated by preliminary measurements (Rush, 1967) of total neutron cross sections as a function of neutron wavelength (Rush, Taylor & Havens, 1962; Rush & Taylor, 1964) which indicate that the NH_3OH^+ ions in phase A have a low barrier (of the order of 1 kcal) to either one- or three-dimensional rotation at room temperature. This rotation is expected to persist well below −150°C.

The N and O atoms show no greater thermal motion than the O's in the ClO_4^- groups (Table 3) so any such rotation is obviously approximately about the N–O
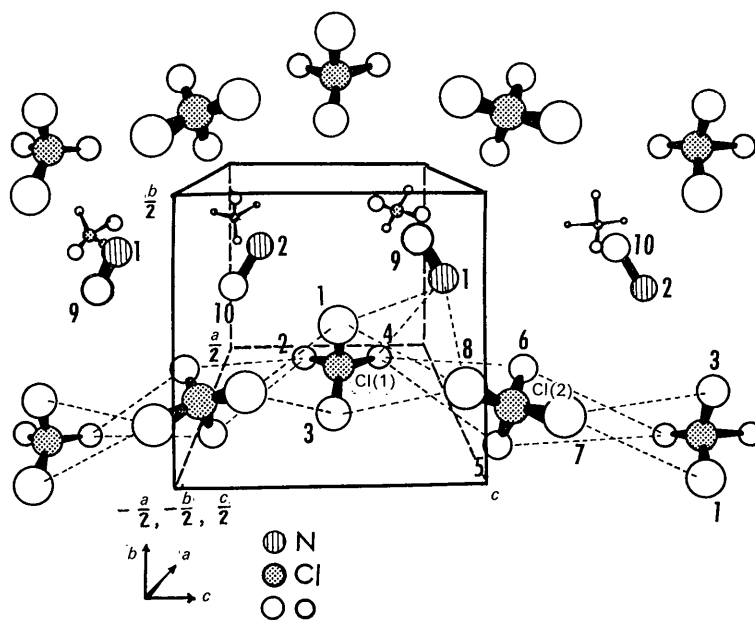

Fig. 1. The crystal structure of HAP.

vector. It is proposed* to examine possible partial or complete rotation about the N–O vector in the various HAP phases of either the complete NH_3OH^+ group or the $-NH_3^+$ group by further subthermal neutron scattering experiments.

Other phases of HAP: phase B

If a single crystal of phase A in an extinction position is heated on the hot stage of the polarizing microscope to about 55°C it cracks and develops 'polarization colors'. X-ray examination of a single crystal of HAP before and after the cracking, and especially of a single crystal of the phase produced above 55°C by repeated recrystallization at 85°C from the melt (melting point 89–91°C), showed that the cracking is a result of a first order phase transformation from phase A to a second phase, phase B. To grow phase B and subsequently examine the crystal on the precession camera, it has been found convenient to seal a crystal of phase A in a 0·2 mm diameter glass capillary and keep it on the camera in a stream of air heated to 85°C by a nichrome wire heating coil in the glass tube delivery nozzle. The solid may be recrystallized by melting it from each end alternately with a small soldering iron. A very small part of the solid should be left unmelted each time to act as a seed. When phase B was cooled to room temperature, after annealing for one hour

at 85°C, and then warmed up past 60°C, it did not crack or develop polarization colors before melting at 90°C. Phase B is monoclinic with the unit-cell parameters given in Table 1. It is related to phase A (cell dimensions at room temperature $a = 7·52$, $c = 15·99$ and $b = 7·13$ Å) since the c of phase A increases by $\frac{3}{2}$ and becomes the b axis of phase B. This was substantiated by comparing precession and Weissenberg photographs of the cracked crystal with those of the parent crystal.
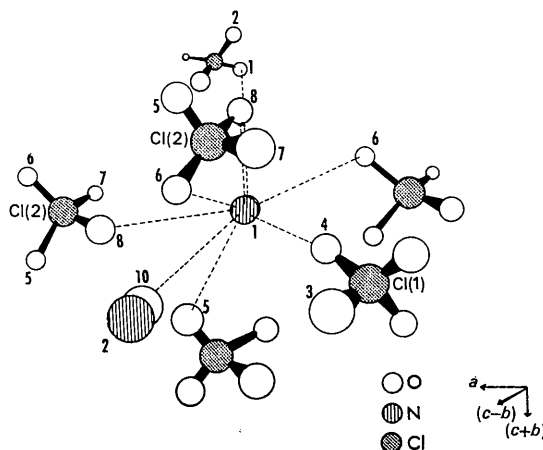

Fig. 2. The environment of the N(1)–O(9) NH_3OH^+ group
The dotted lines represent N(1)–X distances quoted in Table 5

Table 4. Intra-ionic distances and angles in phase A of HAP

ClO_4^- group 1

Atoms	Distance	Atoms	Angle
Cl(1)–O(1)	1·476 (8) Å	O(1)–Cl(1)–O(2)	108·4 (4)°
Cl(1)–O(2)	1·444 (3)	O(1)–Cl(1)–O(3)	107·1 (5)
Cl(1)–O(3)	1·444 (8)	O(1)–Cl(1)–O(4)	109·6 (4)
Cl(1)–O(4)	1·434 (7)	O(2)–Cl(1)–O(3)	110·9 (4)
O(1) –O(2)	2·37 (1)	O(2)–Cl(1)–O(4)	109·4 (5)
O(1) –O(3)	2·35 (1)	O(3)–Cl(1)–O(4)	111·3 (4)
O(1) –O(4)	2·38 (1)		
O(2) –O(3)	2·38 (1)		
O(2) –O(4)	2·35 (1)		
O(3) –O(4)	2·38 (1)		

ClO_4^- group 2

Atoms	Distance	Atoms	Angle
Cl(2)–O(5)	1·435 (7)	O(5)–Cl(2)–O(6)	109·3 (4)
Cl(2)–O(6)	1·445 (7)	O(5)–Cl(2)–O(7)	108·7 (4)
Cl(2)–O(7)	1·433 (8)	O(5)–Cl(2)–O(8)	108·9 (4)
Cl(2)–O(8)	1·455 (7)	O(6)–Cl(2)–O(7)	110·6 (4)
O(5) –O(6)	2·35 (1)	O(6)–Cl(2)–O(8)	109·5 (4)
O(5) –O(7)	2·33 (1)	O(7)–Cl(2)–O(8)	109·8 (5)
O(5) –O(8)	2·35 (1)		
O(6) –O(7)	2·37 (1)		
O(6) –O(8)	2·37 (1)		
O(7) –O(8)	2·36 (1)		

NH_3OH^+

N(1)–O(9)	1·414 (8)	
N(2)–O(10)	1·406 (8)	

The standard errors are those obtained from the parameter errors from the final full-matrix least-squares refinement and the errors in the cell dimensions.

The 24 Å spacing was along the direction which had previously been 16 Å and the phase A $hk0$ reciprocal lattice plane had split into two $h0l$ planes, with a common **c** in the monoclinic phase B. The equivalent cell volumes and hence the densities of the two phases are equal within 0·5 %. Phase B can exist as a clear single crystal from minutes to perhaps two days at room temperature, provided the crystal has been annealed at about 75 °C and cooled slowly to room temperature. In the X-ray beam it gradually becomes cloudy even when held between 60 °C and 90 °C, and after a week gives only a powder pattern. The phase into which it changes at these temperatures has not been established. Good crystals of phase B (and phase C) can be regrown from a crystal which has become cloudy and gives only a powder pattern, which suggests that only a change in phase has taken place. An attempt to supercool a single crystal of phase B fairly slowly to liquid nitrogen temperatures, to freeze the crystal as phase B, produced only a powdered phase.

Fig. 3. The environment of the N(2)–O(10) NH_3OH^+ group. The dotted lines represent N(2)–X distances quoted in Table 5.

Phase B has, qualitatively, a high birefringence as does phase A.

Phase C

If the cracked crystal obtained on heating phase A in a capillary is allowed to melt entirely, then on over 50% of the occasions it will not solidify until below 57–58 °C when it forms a solid melting at 57–58 °C. Single crystals of this phase (phase C) have been grown in capillaries from a completely molten sample of HAP and have been shown to be monoclinic with the unit cell parameters in Table 1. The calculated density is 2·26 g. cm^{-3}. This phase, like phase A, has an axis of nearly 16 Å, which is the unique monoclinic axis. The cell is most easily indexed as face-centered or body-centered. Phase C will persist at room temperature for a few minutes.

The determination of the crystal structures of phases B and C has not been attempted because of their instabilities and presumed high thermal motion, although it is feasible especially if the data are collected rapidly by an automated system.

The metastability of the phases B and C at room temperature suggests that oscillation of the perchlorate groups is not the determining factor in the transition.

Most of the calculations were done with the use of the *X-ray* 63 crystallographic computing system assembled under the editorship and guidance of J. M. Stewart, University of Maryland. A. L. Milstead of the Naval Ordnance Station, Indian Head, Maryland, 20640, helped with the visual estimation of the raw X-ray intensity data.

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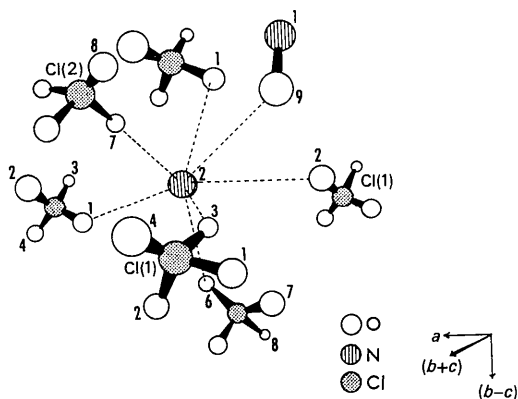
Table 5. *Inter-ionic distances* in phase* A *of* HAP

NH_3OH^+ group 1 [N(1)–O(9)]		NH_3OH^+ group 2 [N(2)–O(10)]	
Atoms	Distance	Atoms	Distance
O(9)–O(5)	2·75 Å	O(10)–O(2)	2·83 Å
O(9)–O(3)	2·78	O(10)–O(5)	2·86
O(9)–O(1)	2·96	O(10)–O(6)	3·01
O(9)–O(2)	3·00	O(10)–N(1)	3·09
O(9)–O(5)	3·08	O(10)–O(8)	3·10
O(9)–O(7)	3·09	O(10)–O(1)	3·11
O(9)–N(2)	3·09		
N(1)–O(4)	2·88	N(2)–O(3)	2·82
N(1)–O(8)	2·94	N(2)–O(6)	2·88
N(1)–O(1)	2·94	N(2)–O(2)	2·91
N(1)–O(6)	2·99	N(2)–O(1)	2·92
N(1)–O(5)	3·02	N(2)–O(7)	2·97
N(1)–O(8)	3·05	N(2)–O(1)	3·04
N(1)–O(6)	3·05	N(2)–O(9)	3·09
N(1)–O(10)	3·09		
N(1)–O(5)	3·17		

* All standard errors are 0·01 Å.

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The Structure of $C_9Cl_7(COOH).(O_2C_2H_4)$, a Condensed Cage Pentacyclononane Compound, Determined by the Symbolic Addition Method*

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The crystal structure of $C_9Cl_7(COOH).(O_2C_2H_4)$, a pentacyclononane derivative, was studied to obtain information on the configuration of the basic carbon cage structure which can be derived from a cube by adding one apex carbon atom. The crystal is monoclinic and the cell constants are: $a = 17.496 \pm 0.004$, $b = 8.005 \pm 0.003$, $c = 24.193 \pm 0.004$ Å, $\beta = 95.6 \pm 0.1°$; the space group is $I2/a$. Three-dimensional intensity data were collected on the CCXD, a computer-controlled diffractometer, which is operated by an IBM 1620 under a stored data-collection program. The crystal structure was determined by systematic application of the symbolic addition method and refined by a full-matrix least-squares program on an IBM 7094. The molecule can be called 6,6-ethylenedioxyheptachloropentacyclo-[5.2.0.0^{2,5}.0^{3,9}.0^{4,8}]nonane-3-carboxylic acid. The configurations of the cyclobutane and cyclopentane rings in the condensed cage molecule are discussed in detail. The carboxyl group is involved in the formation of centrosymmetric dimers which are stacked in the structure with the usual van der Waals contacts.

Introduction

Scherer, Lunt & Ungefug (1965) reported ring contraction through Favorskii rearrangement of chlorinated pentacyclodecanones by the action of alkali on I and III. In each case a pentacyclononane carboxylic acid has been formed (see Fig. 1). The position of the carboxyl group in IV could be uniquely assigned since the starting decanone possesses a symmetric cage structure; whereas for II the choice between the two non-equivalent sites for the group was decided by measuring the *pKa* value of the acid V obtained by a hydrolysis of II which effected a removal of the ethylene glycol residue.

Crystals of II and IV were studied as a part of our continuing effort to determine the shape and size of condensed poly-ring carbon cage structures. Although

IV is a simpler molecule than II, the crystallographic data revealed that there are two non-equivalent molecules per asymmetric unit. This led to determination of the crystal structure of II, which possesses an extra ethylenedioxy group on the apex carbon.

Experimental

Crystals of II, $C_9Cl_7(COOH)(O_2C_2H_4)$, were obtained from CH_2Cl_2 solution of the sample supplied by Professor K. Scherer. One such crystal was ground into an approximately spherical shape and mounted on a G. E. Goniostat on CCXD, a computer-controlled diffractometer system, operated by an IBM 1620 in a closed-loop manner (Cole, Okaya & Chambers, 1963). The crystallographic constants were measured on the diffractometer and used as input parameters to the subsequent data-collection program; the values were $a = 17.496 \pm 0.004$, $b = 8.005 \pm 0.003$, $c = 24.193 \pm 0.004$ Å,

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* The experimental part of this work was performed at IBM Research Center, Yorktown Heights, New York.