

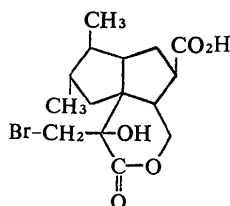
The Crystal and Molecular Structure of the Hemiacetonate of the Bromohydrin of Tetrahydropentalenolactone*

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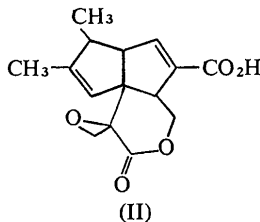
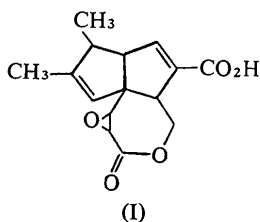
The crystal structure of the hemiacetonate of the bromohydrin of tetrahydropentalenolactone, $C_{15}H_{21}O_5Br \cdot \frac{1}{2}(C_3H_6O)$, has been determined and refined on the basis of three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $C2$, with cell dimensions $a=19.007$, $b=7.886$, $c=12.223$ Å, $\beta=102.47^\circ$. The structure was determined by the heavy-atom method and was refined to an R index of 0.077 for 1818 reflections collected on a 4-circle diffractometer. Anomalous dispersion effects were used to determine the absolute configuration of the molecule. The resultant structure (shown below) firmly establishes the structure of the antibiotic pentalenolactone:



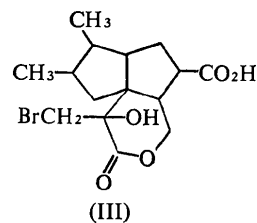
The structure has an interesting packing arrangement with the acetone molecule on a twofold axis and the disordered carboxyl group hydrogen bonding across another twofold axis. The hydroxyl group forms a hydrogen bond to the lactone carbonyl oxygen atom of the molecule related by a twofold screw axis.

Introduction

Recently, structure (I) was proposed for the antibiotic pentalenolactone by Takeuchi, Ogawa & Yonehara (1969). While analyzing this structure at Upjohn, an alternate structure (II) was found that also fitted the



spectral data and that was favored by this data. This evidence led Dr D. G. Martin to prepare the crystalline bromohydrin of tetrahydropentalenolactone (III) for the X-ray analysis reported here. This analysis firmly established (III) as the bromohydrin structure; hence, II is the structure of pentalenolactone. The X-ray study



also served to establish the absolute configuration of the antibiotic. A report containing chemical, spectroscopic, and preliminary X-ray data has already been published (Martin, Slomp, Mizsak, Duchamp & Chidester, 1970). This paper presents a complete report of the X-ray investigation.

Experimental

Crystals of the bromohydrin of tetrahydropentalenolactone, supplied by Dr D. G. Martin, were clear, colorless, and in the form of thick plates. Precession and Weissenberg photographs were used for initial alignment and verification of crystal quality. The photographs indicated the crystals were monoclinic; absence of reflections with $h+k$ odd indicated C -centering - space groups: $C2$, Cm , and $C2/m$. The

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latter two may be ruled out since the compound is optically active. Accurate cell parameters were determined automatically using the precision unit-cell determination procedure of the *UPACS* computerized diffractometer system (Duchamp, 1971); the parameters were obtained by a least-squares calculation based on 19 very accurately determined $K\alpha_1 2\theta$ values for 19 selected high-angle reflections (λ Cu $K\alpha_1 = 1.5405 \text{ \AA}$). Density was measured by flotation in mixed solvents. Initially, the crystals were thought, on the basis of density, to be a dihydrate; however, the X-ray results (and subsequent analytical and spectroscopic measurements) showed it to be a hemiacetonate. The crystal data are listed in Table 1.

Table 1. *Crystal data*

$C_{15}H_{21}O_5Br \cdot \frac{1}{2}(C_3H_6O)$ Space group <i>C2</i>	
F.W. = 390.3	$F(000) = 808$
Monoclinic	
$a = 19.007 (2) \text{ \AA}$	$V = 1788.8 (2) \text{ \AA}^3$
$b = 7.886 (1)$	$Z = 4$
$c = 12.223 (1)$	$D_m = 1.453 \text{ g.cm}^{-3}$
$\beta = 102.47 (1)^\circ$	$D_c = 1.443$
μ Cu $K\alpha = 38.2 \text{ cm}^{-1}$	

Three-dimensional intensity data were gathered on the *UPACS* computerized diffractometer system (a GE diffractometer with an Electronics and Alloys full-circle orienter, Datex automated, controlled by an IBM 1800 computer). The crystal used was $0.06 \times 0.3 \times 0.4 \text{ mm}$ in size. The crystal orientation was determined by the computer before the data collection, using five orienting reflections. Nickel-filtered Cu K radiation was used. The θ - 2θ scan technique was employed with 4° scans at $4^\circ/\text{min}$ and with 10 sec back-

ground counts at each end of the scan. All reflections with $2\theta \leq 140^\circ$ were measured. Five reflections were monitored periodically during the data collection. A general downward trend in intensity of the check reflections was observed; at the end of the data collection, the intensity drop in check reflections ranged from 12% for 025 to 31% for 440. Pictures of the crystal taken under a microscope shortly after data collection show several localized opaque areas. The axial system used to define real-space coordinates and reflection indices is left-handed.

Intensity data were corrected for deterioration using an isotropic time-dependent function with four terms obtained by least-squares fit of the deterioration data for the check reflections. Standard deviations in observed intensities were approximated by the function

$$\sigma^2(I) = \sigma_{\text{counting statistics}}^2 + (0.0394I)^2,$$

where the coefficient of I in the last term was calculated from those deviations in the check reflection observations (after deterioration correction) which were not explained by counting statistics. The usual Lorentz and polarization corrections were applied. An absorption correction was applied using the method of Busing & Levy (1957); transmission factors for observed intensities ranged from 0.78 to 0.34. Reflections for which the scaled background counts exceeded the scan counts were entered as negative intensity observations. The final reduced set contains 1818 reflections.

Trial structure and preliminary refinement

Coordinates of the bromine atom were easily derived from prominent vector peaks in a three-dimensional Patterson map. An electron-density calculation, phased

Table 2. *Final atomic parameters and their standard deviations (in parentheses)*

All values for anisotropic atoms have been multiplied by 10^5 . For isotropic atoms, coordinate parameters have been multiplied by 10^4 . The expression for the anisotropic temperature factors is of the form:

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

The y coordinate of Br was held fixed because of the polar space group. The coordinates are relative to a left-handed system.

	x	y	z	B11	B22	B33	B12	B13	B23
BR	5795(6)	98510(0)	40745(7)	811(5)	3411(26)	1160(8)	15(23)	135(9)	1041(28)
O1	17995(31)	113849(72)	63790(43)	655(23)	1757(98)	1132(43)	332(86)	816(54)	911(113)
C1	19879(39)	96806(113)	62245(49)	560(27)	1662(132)	842(46)	-40(131)	675(61)	291(65)
C2	26444(46)	96212(92)	57132(57)	687(33)	1304(139)	1029(54)	23(131)	697(73)	183(59)
O2	26632(36)	86675(87)	48515(44)	767(27)	2768(126)	1016(45)	150(103)	853(59)	-26(124)
O3	32295(31)	104584(78)	62478(46)	596(22)	2367(127)	1224(45)	-149(89)	651(54)	404(119)
C4	32513(44)	109524(117)	73986(69)	519(33)	2122(173)	1244(71)	-424(127)	564(82)	-139(183)
C4A	29823(44)	94833(105)	79736(59)	531(29)	2008(176)	956(53)	132(123)	461(62)	-288(159)
C5	34424(43)	78096(115)	80212(63)	539(32)	2083(157)	945(58)	-51(135)	492(72)	-263(167)
C6	29254(51)	64192(113)	82003(62)	653(37)	1911(158)	973(61)	265(137)	457(80)	525(168)
C6A	22891(47)	6937(96)	74815(57)	642(33)	1560(139)	766(50)	-78(139)	622(70)	-126(137)
C7	15625(53)	64093(113)	79442(62)	736(40)	1985(154)	882(57)	-11(164)	524(82)	169(167)
C8	15003(51)	78297(121)	87580(65)	670(35)	2215(160)	990(60)	-137(151)	855(80)	-82(180)
C9	16380(45)	94253(101)	81247(60)	602(31)	2020(176)	966(54)	124(125)	746(71)	-232(153)
C9A	22026(47)	89221(102)	74375(57)	575(31)	1744(140)	759(51)	-137(118)	444(69)	-94(142)
C10	13447(48)	87483(115)	55026(64)	617(35)	2089(159)	888(55)	-202(131)	363(74)	368(160)
C11	16010(53)	46065(127)	84053(69)	736(37)	2042(176)	1308(69)	-297(164)	614(86)	359(121)
C12	7899(47)	7850(161)	9157(99)	849(56)	2876(249)	2346(50)	-330(217)	202(161)	-923(325)
O4	5000(0)	113390(131)	5000(0)	764(61)	6819(606)	6932(450)	0(0)	276(283)	169(0)
CA	5000(0)	97081(398)	5000(0)	865(85)	3114(456)	6307(542)	0(0)	-980(336)	0(0)
CAM	4938(63)	92079(239)	61334(139)	676(48)	6869(607)	3131(186)	-2388(286)	718(160)	-3117(567)

	x	y	z	B
CC1	4059(9)	7809(28)	8904(14)	4.26(0.27)
O1C1	4508(9)	9202(23)	8959(14)	9.48(0.36)
O2C1	4185(7)	7002(18)	9741(11)	7.75(0.28)
CC2	4223(14)	7977(53)	8730(23)	8.92(0.53)
O1C2	4344(9)	9082(23)	9441(13)	9.09(0.34)
O2C2	4605(9)	6811(23)	8692(12)	9.61(0.36)

with the bromine, gave 14 additional trial atoms. A second three-dimensional electron-density map yielded all but the carboxyl oxygen atoms and the solvent atoms. At this point, the R index ($R = \sum ||F_o| - |F_c|| / \sum F_o$) was 0.251.

After several cycles of least-squares refinement with the bromine atom anisotropic and other atoms isotropic, an electron-density map showed that the carboxyl oxygen atoms were twofold disordered, giving two positions for the carboxyl group differing by rotation about the molecule-to-carboxyl-carbon bond. The arrangement is such that the carboxyl in one position is in the usual carboxyl-to-carboxyl hydrogen-bonding arrangement, with the carboxyl in the other position related by a twofold axis. With this in mind and from the appearance of the electron-density peaks, equal occupancy was assumed for the two positions. Electron-density maps were calculated in the planes of the carboxyl groups to obtain accurate oxygen positions.

During the ensuing refinement, several trial positions for solvent atoms – then thought to be two water molecules – were tried. Finally, a difference electron-density map was obtained that appeared to show an

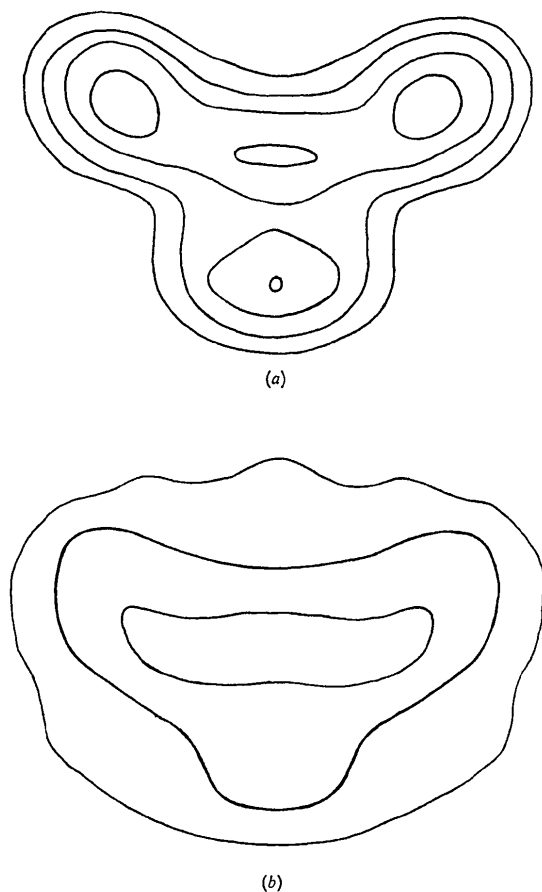


Fig. 1. Electron density (a) and difference electron density (b) in the acetone region. Contours are at intervals of $0.5 \text{ e.}\text{\AA}^{-3}$ beginning at $0.5 \text{ e.}\text{\AA}^{-3}$.

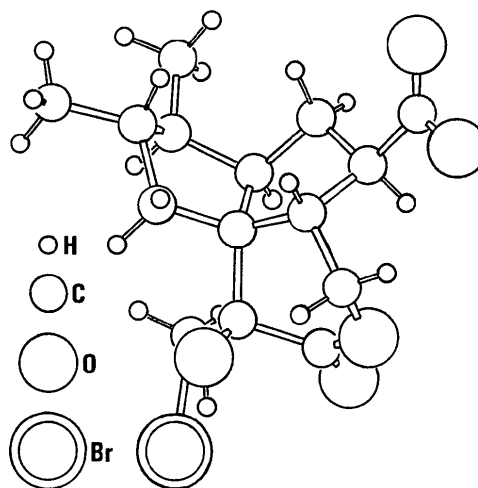


Fig. 2. Absolute configuration and conformation of tetrahydropentalenolactone bromohydrin. Asymmetric carbon atoms C(1), C(4A), and C(8) have the S configuration; C(5), C(6A), C(7), and C(8) have the R configuration by the rules of Cahn, Ingold & Prelog (1966).

acetone molecule lying on the twofold axis at $x = \frac{1}{2}$, $z = \frac{1}{2}$. (The crystals were prepared from an acetone-water mixture.) A check by analytical and spectroscopic measurements was consistent with $\frac{1}{2}$ acetone per parent molecule. Refinement was continued with the acetone included. The symmetry axis of the acetone molecule was assumed to coincide with the twofold axis; therefore, the oxygen and carbonyl carbon atoms were located on the twofold axis and, hence, have a multiplicity of 2.

At this point continuing in the refinement, all atoms were anisotropic except the carboxyl oxygen and acetone atoms. Hydrogen atoms attached to carbon atoms of the molecular skeleton were included in the structure-factor calculation, but were not refined. Hydrogen positions were obtained by calculation based on standard tetrahedral geometry, with methyl hydrogen atoms in staggered positions. All hydrogen atoms were given isotropic temperature parameters (B) of 5.0. After two cycles, the anisotropic thermal ellipsoid of the carboxyl carbon atom became very elongated, so this atom was split into two equal-occupancy disordered positions about 0.5 \AA apart, obtaining much more nearly planar carboxyl groups. Separate isotropic thermal parameters were assigned to each disordered position. Anisotropic thermal parameters were added for the acetone atoms. Refinement converged with an R of 0.088.

Absolute configuration and final refinement

With the anomalous dispersion contribution from the bromine atom included, structure factors were calculated for both enantiomorphs. The R indices for the complete data sets did not differ significantly (0.088 and 0.089). A computer search was made for the 50

reflections most affected by anomalous dispersion. The R values computed for these reflections were 0.124 and 0.185 respectively for the two enantiomorphs, clearly in favor of the first. From this set, 15 reflections were selected for accurate intensity measurements of the reflections and of their Friedel-related counterparts, according to the method of Bijvoet (1955). The crystal used was the same one as in the data collection. Also, scans were as in the data collection, except at $\frac{1}{2}^\circ/\text{min}$ with 200 sec background counts. Each of the 15 pairs clearly agreed with the R index indication.

Using coordinates for the correct enantiomorph, refinement continued with the anomalous dispersion component included. The methyl-hydrogen positions were checked by calculating difference electron-density maps in the planes of the expected atoms. The positions found in the maps were in good agreement with the assumed positions. Also, by difference electron density, the hydroxyl hydrogen atom was located. No attempt was made to locate the carboxyl hydrogen atom (because of disorder) or the acetone hydrogen atoms (because of very high thermal parameters).

Because of storage limitations in the available computer, refinable parameters were split into separate matrices as follows: one matrix for all coordinates; one matrix for isotropic temperature factors of the carboxyl atoms, a scale factor, a secondary extinction parameter (Larson, 1967), and the anisotropic temperature parameters of the Br atom; and individual 6×6 block matrices for the remaining anisotropic thermal-parameter sets. Refinement was considered converged when all parameter shifts were less than $\frac{1}{3}$ standard deviations except for a few carboxyl and acetone parameter shifts (which were only slightly less than standard deviations and were oscillating). The final R index was 0.077, and the standard deviation of fit, $[\sum w(F_o^2 - F_c^2)^2 / m - s]^{1/2}$, was 1.98. Table 2 gives the final atomic parameters and their standard deviations. Hydrogen-atom parameters (not refined) are given in Table 3. Structure factors are listed in Table 4. Fig. 1 shows the

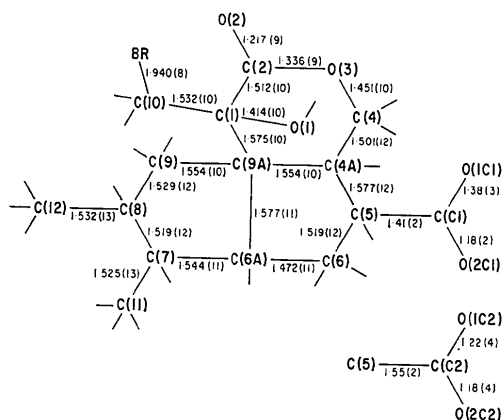


Fig. 3. Bond distances (Å) and standard deviations (in parentheses) of the last reported digit.

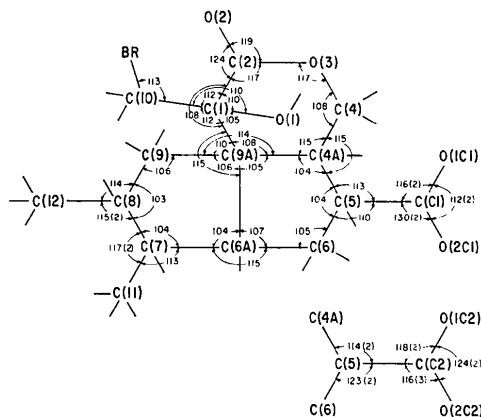


Fig. 4. Bond angles ($^\circ$). Standard deviations are 1° unless indicated otherwise (in parentheses following the angle).

electron density of the acetone region. At the conclusion of the refinement, electron density and difference maps were calculated in the region of the acetone molecule (Fig. 1). Note that the difference density [Fig. 1(b)], calculated with the acetone contributions omitted from F_c but phased from the final parameters of the remaining atoms, does not show resolution of the acetone atoms.

Table 3. Hydrogen coordinates (not refined)

H(O1)	0.17852	1.17844	0.55936
H(4A)	0.37577	1.12325	0.77844
H(4B)	0.29366	1.19637	0.74142
H(C4A)	0.30155	0.99816	0.87354
H(5)	0.36203	0.75766	0.73260
H(6A)	0.28895	0.63703	0.90040
H(6B)	0.30868	0.52931	0.79689
H(C6A)	0.22049	0.63101	0.67514
H(7)	0.11078	0.63295	0.73556
H(8)	0.18532	0.76962	0.94886
H(9A)	0.11826	0.98142	0.76135
H(9B)	0.18326	1.03536	0.86627
H(10A)	0.09488	0.86956	0.59237
H(10B)	0.14989	0.75718	0.53585
H(11A)	0.11630	0.43820	0.87360
H(11B)	0.20530	0.44930	0.90340
H(11C)	0.16140	0.37710	0.77780
H(12A)	0.08070	0.70070	0.97700
H(12B)	0.03840	0.75280	0.85080
H(12C)	0.07120	0.90200	0.94460

All calculations were carried out on an IBM 360 computer using the *CRYM* crystallographic system developed by one of the authors (DJJ). Atomic form factors are from *International Tables for X-ray Crystallography* (1962), except for H which was taken from Stewart, Davidson & Simpson (1965). The real and imaginary components of anomalous dispersion for the bromine were calculated according to the parameters of Cromer (1965). The quantity minimized in the least-squares calculation was $\sum w(F_o^2 - F_c^{*2})^2$, where F_c^* is as defined by Larson (1967). Weights w were taken equal to the reciprocals of the variances $\sigma^2(F_o^2)$ determined at data reduction time and scaled by propagation of error through subsequent corrections.

Table 4. Observed and calculated structure factors

Columns within each group contain the values I, 10Fo, 10|Fc|, and alpha (°). A negative Fo indicates a negative observed intensity.

Table with multiple columns containing numerical data for structure factors, including observed intensity (I), calculated intensity (10Fo), absolute calculated intensity (10|Fc|), and phase angle (alpha). The table is organized into groups of columns for each reflection.

Discussion of the structure

The absolute configuration and conformation of the molecule are shown in Fig. 2, which is taken from Martin *et al.* (1970). Bond distances and angles of the tetrahydropentalenolactone bromohydrin are given in Figs. 3 and 4. None of the nondisordered distances differs significantly from normally observed values (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). The lactone C–O distances vary in a manner explainable in terms of resonance involving some double-bond character for the C(2)–O(3) bond. The C(1)–C(2)–O(3)–C(4) and O(2)–C(2)–O(3)–C(4) torsion angles in the lactone are -16 (1) and 164 (1) $^\circ$, respectively, indicating approximate planarity in agreement with the resonance hypothesis. Distances and angles involving the disordered carboxyl group are reasonable when the errors inherent in refining disordered areas are considered. Also, the standard deviations given in Figs. 3 and 4 were calculated from variances only; including covariances may significantly increase the standard deviations in the disordered areas, because parameters in those areas are especially heavily correlated.

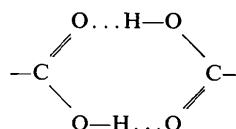
The mean-square deviations and direction cosines in the principal axes of the thermal ellipsoids are shown in Table 5. The major axes of all atoms of the tetrahydropentalenolactone bromohydrin, except for C(12), are approximately along the *a* axis.

Table 5. Mean-square deviations (\AA^2) and direction cosines ($\times 10^4$) of principal axes of the thermal ellipsoids

Atom	MSD	CosA	CosB	CosC	Atom	MSD	CosA	CosB	CosC
Br	0.0675 0.1198 0.1529	0804 -3118 -9467	-5192 -8239 2272	8134 -3948 4272	C(7)	0.0557 0.0663 0.1287	-2238 0985 -9696	-6123 -7883 0612	7887 -6143 -0216
O(1)	0.0511 0.0641 0.1250	-3613 4471 -8183	8900 4271 -1596	3496 -8639 -3525	C(8)	0.0507 0.0693 0.1256	-5395 0538 -8456	-0449 9948 0913	9415 0727 -3292
C(1)	0.0454 0.0526 0.1033	-5040 -0871 8593	-2058 9784 8593	9279 2021 3134	C(9)	0.0480 0.0576 0.1124	-4952 2115 -8427	4513 8914 -0415	8318 -4371 -3422
C(2)	0.0404 0.0535 0.1231	0554 -4337 8693	9845 1737 0221	-1741 9570 2323	C(9A)	0.0507 0.0546 0.1012	-2515 1668 9534	2189 8933 -1115	9748 -2124 0677
O(2)	0.0548 0.0891 0.1390	-4438 -0482 -8949	2484 -9560 -0712	9355 3583 -2370	C(10)	0.0535 0.0735 0.1095	2115 0651 9752	6765 7104 -1941	-7344 6702 -1069
O(3)	0.0619 0.0868 0.1109	4441 4311 -7854	7009 -7132 0048	-6408 -6327 -4347	C(11)	0.0578 0.0938 0.1310	2516 -2610 -9320	9159 3755 1421	-3598 9247 -1244
C(4)	0.0577 0.0794 0.1045	5275 -5069 6817	8410 4247 -3351	-2307 8419 4879	C(12)	0.0636 0.0898 0.2389	-7175 3295 -6137	3062 9406 1470	7658 -1516 -5249
C(4A)	0.0545 0.0723 0.0942	-3358 -2082 -9186	7227 -6824 -1095	6623 7291 -1723	O(A)	0.1336 0.2147 0.5284	9684 0 2495	0 10000 0	0345 0 -9994
C(5)	0.0579 0.0692 0.0962	3019 -3426 -8896	-5885 -8011 1087	-7974 5533 -2410	C(A)	0.0981 0.1297 0.5308	0 9007 -4345	0 10000 0	0 2297 9733
C(6)	0.0517 0.0742 0.1159	-0001 -3294 -5442	8282 5391 -1847	-5472 8347 -0624	C(A'')	0.0642 0.1873 0.3074	7987 5455 2539	5293 -4362 -7277	1070 -8166 5973
C(6A)	0.0470 0.0512 0.1076	-1832 2721 9447	7302 6811 -0545	6823 -7225 1118					

Fig. 5 shows the tribulations required to pack this structure into space group $C2$. A chain of hydrogen bonds occurs along the twofold screw axis at $(\frac{1}{2}, y, \frac{1}{2})$; the hydroxyl of one molecule is hydrogen-bonded to the carbonyl oxygen atom of the lactone of the molecule related by this axis. The hydrogen-bond distance is 2.793 (8) \AA ; the hydroxyl hydrogen position found in the difference map is 2.1 \AA from the lactone carbonyl oxygen atom.

As mentioned previously, the carboxyl group is twofold disordered. One group hydrogen-bonds to the other, related by a twofold axis in the usual carboxyl-to-carboxyl fashion shown below. The hydrogen-



bond distances are 2.60 (2) \AA for O(1C1) to O(1C2) and 2.66 (2) \AA for O(2C1) to O(2C2). Fig. 5 shows one arrangement at the twofold axis at $(\frac{1}{2}, y, 0)$ and the alternate arrangement at the twofold axis $(\frac{1}{2}, y, 1)$.

Torsion angles for the carboxyl groups are given in Table 6. These show that one carboxyl position has the oxygen atom eclipsing C(4A) and the other position has the oxygen atom eclipsing C(6). Plane calculations for the carboxyl groups and the carboxyl-carboxyl pair are given in Table 7. The individual carboxyl groups are planar, considering that the alternate positions for the carboxyl carbon atoms are only 0.43 \AA apart and that a larger spreading yields exactly planar groups. The carboxyl-carboxyl pair is fairly flat.

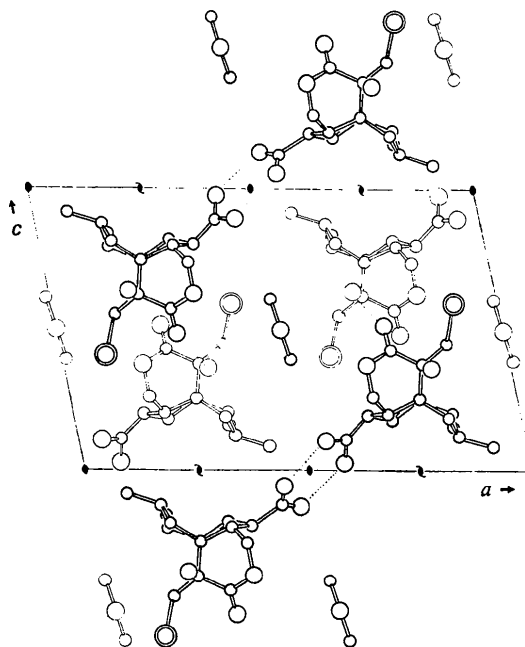


Fig. 5. Packing viewed in projection down the *b* axis. Atoms are designated as in Fig. 2. Dotted lines indicate hydrogen bonds. Axial system is left-handed.

Table 6. *Torsion angles for the carboxyl groups*

Angles are defined as positive for a right-handed screw looking down the atom(2)-atom(3) bond.

Carboxyl position 1	
C(4A)-C(5)-C(C1)-O(1C1)	53 (2) ^o
C(4A)-C(5)-C(C1)-O(2C1)	-110 (2)
C(6)-C(5)-C(C1)-O(1C1)	168 (1)
C(6)-C(5)-C(C1)-O(2C1)	6 (2)
Carboxyl position 2	
C(4A)-C(5)-C(C2)-O(1C2)	-22 (3)
C(4A)-C(5)-C(C2)-O(2C2)	172 (2)
C(6)-C(5)-C(C2)-O(1C2)	104 (3)
C(6)-C(5)-C(C2)-O(2C2)	-60 (2)

Fig. 6 shows the distances and angles in the acetone molecule. Standard deviations are high; all acetone atoms have large anisotropic thermal parameters. Bond distances are within two standard deviations of the much more accurate distances for acetone determined by microwave [Nelson & Pierce (1965); C=O=1.222 (3) Å, and C-C=1.507 (3) Å]. Bond angles, however, are very different from the microwave C-C-C angle of 117.2 (3)^o. As Table 5 shows, both O(A) and C(A) have very large anisotropic components approximately in the plane of the acetone molecule, with mean-square deviations of 0.52 and

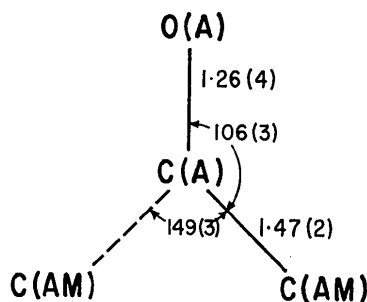


Fig. 6. Bond distances (Å) and angles (^o) in the acetone of solvation. Standard deviations are given in parentheses following the values.

0.53 Å², respectively; the acetone methyl carbon atom, however, has a much smaller principal component in a different direction. Undoubtedly, these thermal effects cause systematic errors in the bond angles calculated from average positions, perhaps enough to account for the discrepancy with the microwave angles.

Short intermolecular contacts are given in Table 8. The acetone oxygen atom makes intermolecular contacts of 3.67 (2) Å to the bromine atom and 3.15 (2) Å to C(10). Whereas the Br-O contact is long compared to 3.35 Å, the sum of the van der Waals radii (Pauling, 1960), the O-C distance is short compared to 3.4 Å [obtained from summing the O and CH₃ radii of Pauling (1960)]. Displacement of the oxygen atom along its principal anisotropic axis would tend to shorten the Br contact while somewhat lengthening the C(10) contact (see Fig. 5). There are no intermolecular contacts to either of the acetone carbon atoms. These considerations preclude the possibility of an acetone disorder, in which the methyl and oxygen atoms are interchanged, since the larger methyl group could not fit in the oxygen position. Probably, the solvent is undergoing a rather complicated type of thermal motion, perhaps coupled with the main molecule. The thermal parameters (see Table 5) would agree with a mode in which solvent motion in the *c* direction is coupled with motion of the main molecule in the *a* direction. Obviously, data presented here can either prove nor disprove this suggestion.

Table 8. *Intermolecular distances*

All distances less than 3.5 Å are listed. Distances involving Br are listed to 3.7 Å. Carboxyl-to-carboxyl distances about the twofold axis are excluded. No C-C contacts are less than 3.7 Å.

Related atom	Atom	<i>d</i>	Symmetry
Br	O(2C2)	3.66 (2) Å	$\frac{1}{2}-x, y-\frac{1}{2}, 1-z$
O(1)	O(2)	2.79 (1)	
C(2)	O(2)	3.44 (1)	
O(3)	O(2)	3.31 (1)	
O(A)	Br	3.67 (2)	
O(A)	C(10)	3.15 (2)	
O(1C2)	C(12)	3.47 (2)	$\frac{1}{2}-x, y-\frac{1}{2}, 2-z$

Table 7. *Least-squares planes through carboxyl groups*

Out-of-plane distances are given for atoms used to calculate the planes. Direction cosines are with respect to the real-cell axes.
Asterisked atoms are transformed about the twofold axis near the carboxyl group.

	<i>A</i>	<i>B</i>	<i>C</i>
cos (<i>a</i>)	-0.661	-0.477	-0.588
cos (<i>b</i>)	0.570	-0.534	0.555
cos (<i>c</i>)	0.619	0.785	0.702
<i>d</i> _{origin}	5.22 Å	1.26 Å	6.61 Å
	C(5)	C(5)	C(5)
	0.03 Å	0.02 Å	-0.15 Å
	C(C1)	C(C2)	C(C1)
	-0.08	-0.08	-0.08
	O(1C1)	O(1C2)	O(1C1)
	0.02	0.03	0.07
	O(2C1)	O(2C2)	O(2C1)
	0.03	0.03	0.14
			C(5)*
			-0.24
			C(C2)*
			0.10
			O(1C2)*
			0.11
			O(2C1)*
			0.05

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The Crystal Structures of the Dimethyldicyano Compounds of Silicon, Germanium, Tin and Lead

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The crystal data for the group IV compounds $(\text{CH}_3)_2\text{M}(\text{CN})_2$ are:

	<i>a</i>	<i>b</i>	<i>c</i>	Space group	<i>Z</i>	<i>D</i> _{calc}
$(\text{CH}_3)_2\text{Si}(\text{CN})_2$	13·76 (2) Å	7·44 (1) Å	6·45 (1) Å	<i>Pnma</i>	4	1·11 g.cm ⁻³
$(\text{CH}_3)_2\text{Ge}(\text{CN})_2$	13·64 (2)	7·49 (1)	6·35 (1)	<i>Pnma</i>	4	1·58
$(\text{CH}_3)_2\text{Sn}(\text{CN})_2$	9·00 (2)	9·74 (2)	7·95 (1)	<i>Fmm2</i>	4	1·92
$(\text{CH}_3)_2\text{Pb}(\text{CN})_2$	9·02 (1)	8·37 (2)	8·88(1)	<i>Fmm2</i>	4	2·77

In the Si and Ge compounds, approximately tetrahedral molecules form linear chains through weak acid-base $\text{N}\cdots\text{M}$ interactions. In the Sn compound, and presumably in the Pb compound, stronger $\text{N}\cdots\text{M}$ interactions occur such that planar sheets are formed; each normally tetrahedral molecule is distorted to a more nearly octahedral arrangement by the formation of two additional equivalent $\text{N}\cdots\text{M}$ interactions.

Introduction

Previous work shows that the trimethylcyano compounds of germanium (Schlemper & Britton, 1966*b*), tin (Schlemper & Britton, 1966*a*), and lead (Chow & Britton, 1971) have intermolecular interactions in the solid state that are more specific than van der Waals interactions. In $(\text{CH}_3)_3\text{GeCN}$, discrete molecules interact through a weak donor-acceptor interaction between the lone pair on the nitrogen atom and the germanium atom in the next molecule. In $(\text{CH}_3)_3\text{SnCN}$ (and probably in $(\text{CH}_3)_3\text{PbCN}$), the structure is similar, but the interaction has proceeded to the point where each cyanide group is halfway between two adjacent trimethyltin groups. It has also been observed, in the series $(\text{CH}_3)_{3-n}\text{As}(\text{CN})_n$, that as *n* increases from 1 to 3 the intermolecular $\text{N}\cdots\text{As}$ interaction increases in strength, as evidenced by the shortening of the $\text{N}\cdots\text{As}$ distance (Britton, 1967). We report here the structures of $(\text{CH}_3)_2\text{M}(\text{CN})_2$, where M is Si, Ge, Sn, and Pb. This series was studied to see to what extent the second cyanide group affects the previously observed interactions, *i.e.* whether it merely strengthens them, as

with arsenic, or whether it leads to sixfold coordination, to some degree, around the metal atom. The structures of SnF_4 and PbF_4 (Hoppe & Dahne, 1962) and of $(\text{CH}_3)_2\text{SnF}_2$ (Schlemper & Hamilton, 1966) suggest a model for tetragonally symmetric sixfold coordination around the metal atom [shown later in Fig. 1(c)].

Experimental

Preparation and properties

Dimethyldicyanosilane was prepared by mixing dimethyldichlorosilane with chloroform and placing the solution over AgCN . The mixture was shaken occasionally and allowed to stand for two months. The solution was then filtered and the liquid distilled off under a vacuum. The resulting solid was purified by vacuum sublimation. Peaks were observed at 2195 and 2108 cm^{-1} in the $\text{C}\equiv\text{N}$ region of the infrared spectrum; these may be compared with values 2179 and 2096 cm^{-1} reported by McBride & Beachell (1952). The peak at 2195 cm^{-1} was approximately three times as intense as the one at 2108 cm^{-1} . When the compound was left exposed to the air, it hydrolyzed rapidly and both peaks decreased