

packed face centred lattice (Kihara, 1963). Such an arrangement allows the close approach of negative (nitrogen) atoms and positive groups (methylene groups) of molecules. The hexamethylenetetramine-borine molecules are approximately spherical except for the protrusion of the BH_3 groups. Each molecule is surrounded by six others parallel to it, at a distance of 6.15 \AA between centres. Six other molecules are at 7.64 \AA , and two molecules along the $[111]_{\text{rh}}$ are at 7.82 \AA . This arrangement is somewhat different from that found in hexamethylenetetramine crystals, where each molecule is surrounded by eight others at 6.08 \AA between centres and by six others at 7.02 \AA in a body centred lattice. The α_{rh} value corresponding to body centred cubic packing is $109^\circ 28'$ in comparison with $\alpha = 103^\circ 12'$ for the hexamethylenetetramine-borine crystals.

The nearest distance of C and N atoms from different molecules is 3.82 \AA ; between B and C atoms, 3.94 \AA . The closest approach of the molecular cores, however, is influenced by the nitrogen-to-hydrogen and hydrogen-to-hydrogen contacts of the neighbouring molecules. Forty one such contacts involving a single molecule exist up to the upper limit 3.2 \AA . These contacts most frequently occur with distances of $2.8\text{--}3.0 \text{ \AA}$ ($6\text{N}\cdots\text{H}$ and $27\text{H}\cdots\text{H}$ contacts).

We would like to express our gratitude to Professor H. H. Zeiss, Director of Monsanto Research, for his help and interest in this work. We are greatly indebted

to Dr J. J. Daly and to Dr P. J. Wheatley for their advice and considerable aid. Structure calculations were done on an ELLIOTT 803 computer with programs written at Monsanto Research in Zürich.

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Crystal and Molecular Structure of a Brominated Isofenchone

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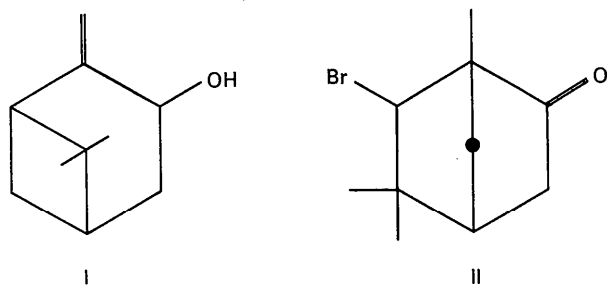
The constitution and configuration of the compound produced by hydrobromination of *trans* pinocarveol has been determined by X-ray diffraction methods, and confirmed as 6-bromoisofenchone. The crystals are orthorhombic, $P2_12_12_1$, with $a = 12.89$, $b = 11.37$, $c = 6.90 \text{ \AA}$; $Z = 4$. Three-dimensional least-squares refinement of 637 reflexions has given a structure ($R = 0.126$) with an average standard deviation of 0.03 \AA in C–C bonds and no significant departures from expected bond lengths. Despite the strain introduced by the keto group, the molecular skeleton is remarkably symmetrical about the median plane. The dihedral angle in each of the 5-membered rings is about 55° .

Introduction

Hartshorn & Wallis (1963) reported that hydrobromination of *trans*-pinocarveol (I) followed by oxidation produced a brominated isofenchone (II) through a rearrangement reaction. The molecular structure of the product was established by degradation methods and

neutron magnetic resonance spectroscopy, but no indication of the stereochemistry of the molecule was obtained. A knowledge of the position of the bromine atom relative to the ring system was essential for determination of the rearrangement mechanism. N.m.r. results suggested the *endo* configuration (I.R.C. McDonald, private communication) but full confirma-

tion of this could be obtained only from an X-ray structure determination.



Since the structure of the molecular skeleton is of interest as an example of a strained system, and as very few molecules with a similar skeleton have been studied by X-ray methods, a three-dimensional study was initiated, although it was appreciated that the stereochemistry could probably have been derived from projections.

A preliminary report of the stereochemistry, obtained largely from one projection, has been published elsewhere (Williams, 1964).

Experimental

Crystals of the compound were kindly provided by Dr M.P.Hartshorn. The crystals were poorly formed, but displayed predominantly the forms {001} and {110}. Measurements of precession and Weissenberg photographs gave the following constants for the orthorhombic cell: $a = 12.89 \pm 0.02$, $b = 11.37 \pm 0.02$, $c = 6.90 \pm 0.02$ Å.

The systematically absent reflexions unequivocally indicated space group No. 19, $P2_12_12_1$, and assuming $Z = 4$, the calculated density is 1.52 g.cm^{-3} , which was roughly checked by observing the behaviour of the crystals in chloroform.

Three-dimensional data hkL , $L = 0$ through 4, were collected by the Weissenberg equi-inclination method, packs of five films being used. The crystals proved to be somewhat volatile, and crystals of a suitable size for intensity data collection lost over half their weight in the fifty hours required to photograph a layer. Therefore a crystal enclosed in a 1 mm bore Pyrex capillary, wall thickness 0.05 mm, was photographed. The $h0l$ layer was photographed to provide correlation between the other layers. Of the 880 independent reflexions theoretically attainable in the volume explored, a total of 637 were observed and measured visually, these representing 52% of the total data accessible to Cu K radiation. The measured intensities were corrected for Lorentz and polarisation effects and put on an approximately absolute scale by Wilson's (1942) method. No corrections were made for absorption, since the magnitude of this effect on a small, approximately spherical crystal was not considered to be great enough to

justify the complex corrections necessary for a crystal in a glass capillary.

The positions of the bromine atoms were located from $P(uv)$ and $P(uw)$ syntheses. A first solution of the structure was obtained from an electron density projection on the xy plane, phased on the bromine atoms, in which most of the light atoms were resolved, and the shape of the molecule clearly shown. The x and y coordinates of the bromine atoms were refined by two cycles of structure factor-difference Fourier calculations, and these coordinates, with the bromine z coordinate from the $P(uw)$ synthesis were used to compute phases for a three-dimensional electron density synthesis. All the light atoms were clearly revealed in the synthesis, even the oxygen atom being distinguishable from the carbons by its greater electron density.

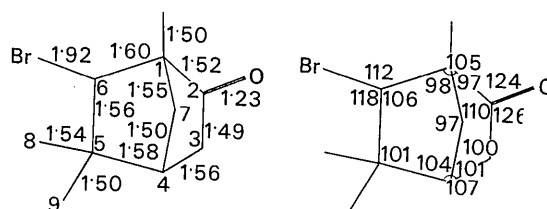


Fig. 1. Bond lengths and angles in bromoisofenchone.

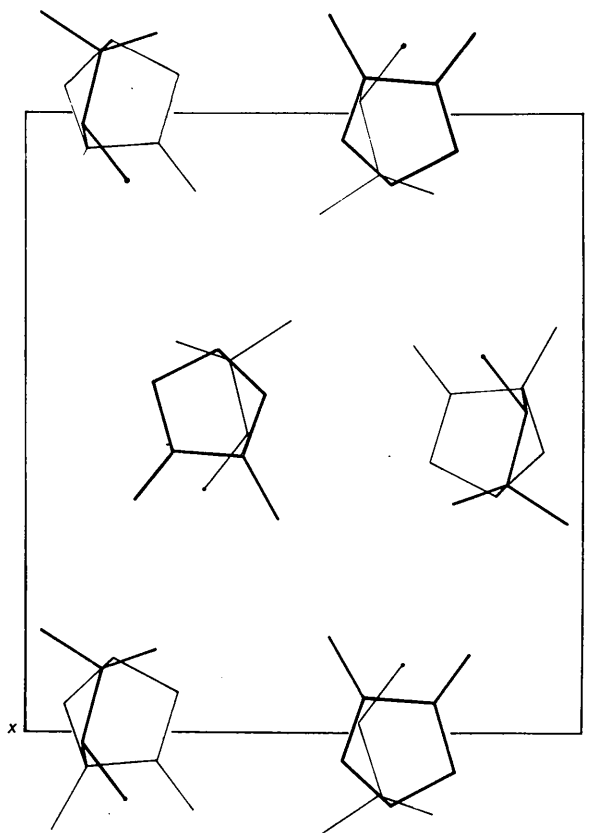


Fig. 2. The structure viewed down the Z axis.

The light atom coordinates were picked off the electron density synthesis, and refined by a block-diagonal, least-squares method, with 3×3 positional and 6×6 or 1×1 temperature factor matrices. A series of nine cycles of refinement was carried out, using the accelerated refinement device due to Hodgson & Rollett (1963), with a T_0^* series of relaxation ('fudge') factors. The temperature factors for the light atoms were all kept isotropic, but the bromine atom had shown pronounced anisotropy in the two and three dimensional electron density syntheses, and was accordingly given anisotropic temperature factors. The stationary atom scattering factors given in *International Tables for X-ray Crystallography* (1962) for bromine, oxygen and carbon were used. Refinement proceeded smoothly, the conventional disagreement index, R , dropping from 0.27 with the original coordinates to 0.126 with the ninth cycle. The adequacy of the weighting scheme was examined periodically during the refinement, and small changes were made to the original scheme as they appeared to be desirable. The scheme finally used was $w=1$ for $F < 28$, $w=28/F$ for $F > 28$. In the ninth cycle the maximum indicated shift was rather smaller than the average standard deviation, and in view of the size of the R value, and the expected accuracy of the data, further refinement was judged to be unwarranted. No attempt was made to include the hydrogen atoms at any stage.

Results

Calculated and observed structure factors are available from the author. The final atomic coordinates and temperature factors from which structure factors were calculated are given in Table 1, and Fig. 1 shows the molecular dimensions and angles. The average standard deviations are 0.025 Å in the C–Br bond, 0.026 in the C=O bond, 0.033 in C–C bonds, and 1.80° in all angles. Fig. 2 depicts the packing of the molecules in the crystal as viewed down the Z axis.

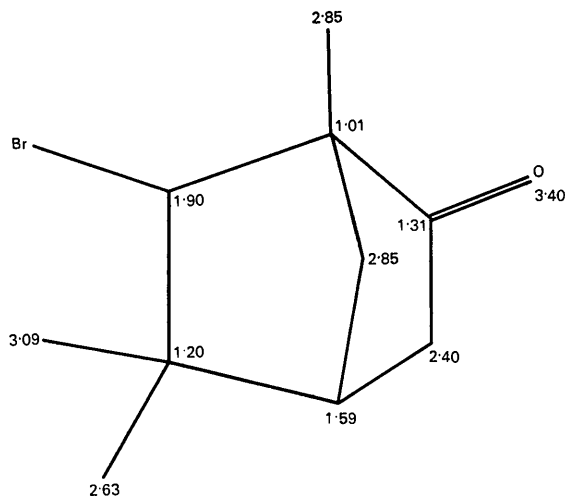


Fig. 3. The variation of isotropic temperature factors of the atoms in the molecule.

Table 1. Final atomic coordinates

	x	y	z	B (Å ²)
C(1)	0.5553	0.3917	0.4747	1.01
C(2)	0.5472	0.2621	0.4237	1.31
C(3)	0.4363	0.2255	0.4172	2.40
C(4)	0.3820	0.3445	0.4691	1.59
C(5)	0.3993	0.3663	0.6925	1.20
C(6)	0.5158	0.4015	0.6940	1.86
C(7)	0.4536	0.4313	0.3732	2.85
C(8)	0.3366	0.4742	0.7578	3.09
C(9)	0.3705	0.2674	0.8261	2.63
C(10)	0.6564	0.4523	0.4317	2.85
O	0.6224	0.1964	0.4012	3.40
Br	0.60693	0.32116	0.87114	

Anisotropic thermal parameters in the expression

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

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Br	0.0052	0.0133	0.0146	-0.0025	-0.0122	0.0022

Discussion

The constitution of the molecule is fully confirmed as 6-bromo-1,5,5-trimethylbicyclo[2,2,1]heptan-2-one, or 6-bromoisofenone. The bromine atom is in the *endo* configuration as was suggested by n.m.r. results. This confirmation of the structure is completely independent of earlier work, as no chemical information was used at any time in determining the crystal structure.

All bond lengths in the molecule appear to be normal; no significant departures from expected lengths are observed. The average C–C bond length is 1.536 Å. The expected shortening of the bonds adjacent to the carbonyl group is only about one standard deviation in these results, and so would not be a significant effect, although one of these bonds [C(2)–C(3)] is apparently the shortest in the molecule (1.488 Å).

The major axis of the vibration ellipsoid of the bromine atom is approximately normal to the C–Br bond, as would be expected if the molecular packing is not predominantly controlled by the bromine atom. The isotropic temperature factors of the light atoms show an interesting variation around the molecular skeleton as shown in Fig. 3. With an expected standard deviation in the isotropic temperature factors of 0.3 Å² the variation of temperature factors around the molecule is probably significant, and suggests that the molecule is vibrating rigidly about an axis running approximately through atoms C(1) and C(5). The direction of the major axis of the bromine vibration ellipsoid supports this, but no meaningful results could be obtained by refining anisotropic temperature factors for other atoms. If a correction had been applied to the intensities for absorption, using Bradley's (1935) data for spherical crystals, the overall temperature factor for the crystal would be expected to be about 0.3 Å² greater than the values given in Table 1, but differences in temperature factor from one atom to another, and the anisotropy of the bromine atom are not expected to be materially in error as a result of neglecting the absorption correction.

Three main planes of atoms occur in the molecule, the equations to which have been determined by the least-squares method of Schomaker, Waser, Marsh & Bergman (1959). Table 2 lists these equations, and the distances of the atoms from the 'best' planes. In these equations, X , Y and Z are coordinates in Å. The oxygen atom lies only about two standard deviations away from the formal C(1),C(2),C(3),C(4) plane, a distance which is probably not significant. The plane C(1),C(4)C(7) bisects the angle between the two main planes of the boat-shaped six-membered ring, the difference between the calculated angles of 56.20° and 55.33° between the C(1),C(2),C(3),C(4) and C(1),C(4),C(7) and the C(1),C(4),C(5),C(6) and C(1),C(4),C(7) planes, respectively, probably being within experimental error. This dihedral angle of about 56° in the five-membered rings does not greatly exceed the angle found by Rérat & Rérat (1964) for the aliphatic five-membered ring in perkinamine, of 51° . The ring in perkinamine is completely free of constraint, and the dihedral angle found seems to be remarkably large for an unstrained five-membered ring. However, if correct, this result for perkinamine suggests that the strain in the fused five-membered rings of the bicyclo[2,2,2]heptane skeleton is not very great.

Table 2. Equations to main planes in the molecule

C(1)C(2)C(3)C(4):					
	$0.50705X - 2.67646Y + 6.69680Z - 2.41260 = 0$				
$D, \text{Å}$	C(1)	C(2)	C(3)	C(4)	0
	-0.001	0.001	-0.001	0.001	0.064
C(1)C(4)C(5)C(6):					
	$3.05529X - 10.94017Y + 0.93279Z + 2.15531 = 0$				
$D, \text{Å}$	C(1)	C(4)	C(5)	C(6)	
	0.009	-0.009	0.014	-0.014	
C(1)C(4)C(7)C(10):					
	$-2.21833X + 7.41983Y + 5.08930Z - 4.09411 = 0$				
$D, \text{Å}$	C(1)	C(4)	C(7)	C(10)	
	-0.004	0.002	0.003	0.001	

The angles in the molecular skeleton, shown in Fig. 4, are all significantly below the normal C-C-C angles found in unstrained aliphatic systems. A striking feature of the distribution of angles in the skeleton is that despite the asymmetry introduced into the skeleton by the keto group, the skeleton retains a considerable degree of pseudosymmetry as a result of the distribution around the rest of the skeleton of the strain introduced by the keto group. Thus the C(1) atom is forced away from the centroid of the skeleton by the adjacent keto group, reducing the angles subtended by C(1) from C(2), C(6) and C(7) below the corresponding angles at C(4) and increasing the angle at C(6) to a value approximating that at C(2). Although the *mm* symmetry of the bicycloheptane skeleton is formally eliminated com-

pletely by the introduction of the keto group, in fact the redistribution of the distortion almost restores part of the symmetry (*m*) to the carbon skeleton.

Previous work on similar carbon skeletons has been carried out by Macdonald & Trotter (1965*a,b*) on *anti*-8-tricyclo[2,2,1,0^{2,4}]octyl *p*-bromobenzenesulphonate and *anti*-7-norbornenyl *p*-bromobenzoate. In these compounds, the bicycloheptane skeleton is modified by a methylene bridge, and by a double bond, respectively, across the 2,3 positions. These structures were studied with the object of measuring the bridgehead angle at the C(7) atom. The values found, of 97° and 96° are, within the experimental error the same as the angle in bromoisofenchone, supporting the conclusion formed by Macdonald & Trotter (1965*b*) that this angle does not change sufficiently to explain the differences in solvolytic activity at this point between their two compounds. The dihedral angles of the five-membered rings are almost identical in all three compounds. If the methylene bridge in the tricyclo-octane derivative is ignored, the symmetry of the bicycloheptane nucleus is very close to *mm*. Comparison of the angles in this skeleton with those in the norbornene and isofenchone compounds (Fig. 4) shows how the strain introduced by the double bond, and the keto group, respectively, is distributed around the ring structures.

No other previous studies appear to have been made of the bicycloheptane structure, the nearest approach to it being the halo- and cyano-camphors studied by Wiebenga & Krom (1946). These compounds have the same basic skeleton as isofenchone, but the accuracy of the determinations does not permit reliable bond angles to be calculated.

The bromoisofenchone molecules are efficiently packed in the X direction of the crystal, the oxygen atom of one molecule fitting neatly into the hollow formed by atoms C(5), C(4), C(8), and C(9) of the next. The O-C(4), O-C(8) and O-C(9) intermolecular distances are all $3.5 \pm 0.1 \text{ Å}$, and are the shortest contacts in the structure. The bromine atom does not appear to play a major part in determining the crystal structure.

The computer programs used in this work were written by Dr Shiono, University of Pittsburgh, for the IBM 650 (intensity reduction, structure factors, 2-D Fourier) and Drs F.R.Ahmed and G.A.Mair, National Research Council, Canada, for the IBM 1620 (S.F.-L.S., 3-D Fourier). The assistance of the Govern-

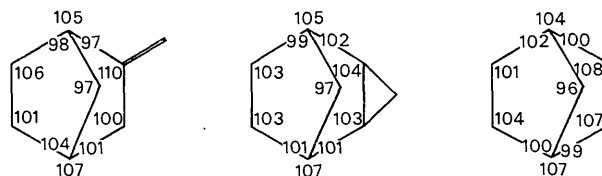


Fig. 4. Bond angles in the skeletons of bromoisofenchone and related compounds.

ment Statistician, J.V.T. Baker, in providing time on the IBM 1620 computer is gratefully acknowledged.

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The Crystal Structure of 2 α -Bromo-5 β -bromomethyl-5 α -methyl-2 β -oxo-1,3,2-dioxaphosphorinane*

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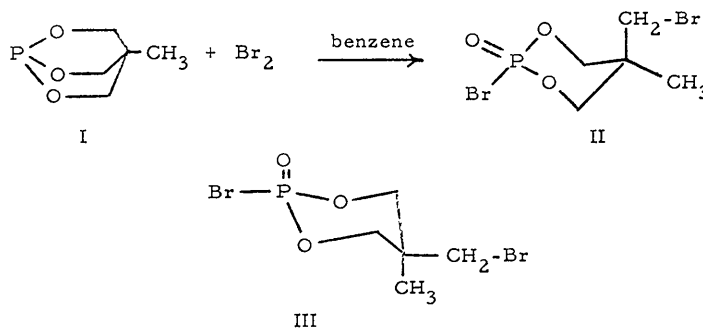
(Received 23 September 1966 and in revised form 15 February 1968)

The crystal structure of 2 α -bromo-5 β -bromomethyl-5 α -methyl-2 β -oxo-1,3,2-dioxaphosphorinane has been determined by three-dimensional single-crystal X-ray diffraction techniques. The crystals are orthorhombic, space group $P2_12_12_1$ with unit-cell dimensions $a=13.415$, $b=11.407$, $c=6.215$ Å and four molecules per unit cell. The final R for 478 reflections is 0.045. The molecular conformation is a distorted chair with the bromo and bromomethyl groups in axial positions. The interior O–P–O angle is 104.9° which is similar to the corresponding angle in acyclic phosphate esters and explains the similarity in the rates of hydrolysis of six-membered cyclic and acyclic phosphate esters as opposed to the strained five-membered cyclic esters.

Introduction

In the course of nuclear magnetic resonance studies on the mechanism of long range phosphorus–hydrogen spin–spin interactions, 2 α -bromo-5 β -bromomethyl-5 α -methyl-2 β -oxo-1,3,2-dioxaphosphorinane (II, hereafter referred to as BBMOD) was prepared by reaction in benzene of the bicyclic phosphite ester (I) with bromine (Bertrand, Verkade & McEwen, 1968). Prior to the

present work neither the conformation of BBMOD nor the mechanism of the reaction had been established. The dipole moment of BBMOD in dioxane is 6.59D which agrees favorably with the 6.40D moment calculated for conformation II from individual bond moments. An identical treatment of individual bond moments for the other, sterically more favorable chair conformation (III) yielded a calculated moment of 1.57 D.



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In order to provide the structural parameters necessary for the interpretation of both the ³¹P and the proton spectra of BBMOD, and to confirm the conformation tentatively assigned on the basis of the dipole