2941 reflections
136 parameters
H atoms riding, C—H =
   0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 0.1064P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
C1	0.6554 (2)	0.46352 (14)	0.72286 (14)	0.0344 (3)
C2	0.5261 (2)	0.37590 (15)	0.8102 (2)	0.0407 (3)
C3	0.3320 (2)	0.4311 (2)	0.8827 (2)	0.0412 (3)
C4	0.2790 (2)	0.5885 (2)	0.87007 (15)	0.0382 (3)
C5	0.3934 (2)	0.68110 (14)	0.78238 (14)	0.0333 (3)
C6	0.5691 (2)	0.61730 (14)	0.68736 (15)	0.0399 (3)
O1	0.2124 (2)	0.35140 (14)	0.9597 (2)	0.0660 (4)
O2	0.6329 (3)	0.68388 (14)	0.57901 (14)	0.0756 (5)
N1	0.8482 (2)	0.41617 (13)	0.66042 (13)	0.0429 (3)
C7	1.0069 (2)	0.5047 (2)	0.57713 (14)	0.0389 (3)
C8	0.9209 (3)	0.2649 (2)	0.6892 (2)	0.0552 (5)
C10	0.3479 (2)	0.84453 (14)	0.76812 (15)	0.0386 (3)
C11	0.5585 (2)	0.91824 (14)	0.77722 (15)	0.0667 (6)
C12	0.2509 (2)	0.89601 (14)	0.62999 (15)	0.0610 (5)
C13	0.1859 (3)	0.8905 (2)	0.8861 (2)	0.0601 (5)

Table 2. *Selected geometric parameters* (Å, °)

C1—N1	1.358 (2)	C5—C10	1.527 (2)
C1—C2	1.364 (2)	C6—O2	1.214 (2)
C1—C6	1.512 (2)	N1—C8	1.458 (2)
C2—C3	1.431 (2)	N1—C7	1.464 (2)
C3—O1	1.236 (2)	C7—C7^i	1.520 (3)
C3—C4	1.478 (2)	C10—C13	1.531 (2)
C4—C5	1.343 (2)	C10—C11	1.533 (2)
C5—C6	1.497 (2)	C10—C12	1.535 (2)
N1—C1—C2	123.04 (12)	O2—C6—C1	119.96 (12)
N1—C1—C6	119.41 (11)	C5—C6—C1	118.89 (11)
C2—C1—C6	117.39 (12)	C1—N1—C8	118.39 (12)
C1—C2—C3	121.71 (13)	C1—N1—C7	126.67 (11)
O1—C3—C2	121.74 (14)	C8—N1—C7	114.58 (12)
O1—C3—C4	119.26 (13)	N1—C7—C7^i	111.0 (2)
C2—C3—C4	118.94 (12)	C5—C10—C13	110.67 (12)
C5—C4—C3	122.69 (12)	C5—C10—C11	109.68 (11)
C4—C5—C6	116.92 (12)	C13—C10—C11	107.62 (14)
C4—C5—C10	124.52 (12)	C5—C10—C12	110.74 (12)
C6—C5—C10	118.47 (11)	C13—C10—C12	107.99 (13)
O2—C6—C5	120.99 (12)	C11—C10—C12	110.07 (12)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Methyl H atoms were located using difference Fourier syntheses with toroidal averaging and were included in subsequent calculations as a group with idealized tetrahedral geometry riding on the methyl C atom. The positions of all other H atoms were calculated and constrained to ride on their respective C atoms.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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7,7-Dibromo-3-dibromomethylene-2,2-dimethylnorbornan-1-ol

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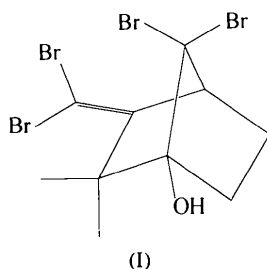
Abstract

The X-ray structure of the title compound, $C_{10}H_{12}Br_4O$, which is a by-product of 3,3-dibromocamphor bromination, confirms the structure predicted on the basis of spectroscopic data. The geometry of the molecular skeleton (a six-membered boat and two five-membered envelopes) does not differ significantly from those of other norbornane derivatives (norbornane is bicyclo[2.2.1]heptane). O—H···Br intermolecular hydrogen bonds link the molecules to form infinite chains along the [100] direction. The pattern of the non-bonding contact distances can be used for discussing similar interactions in the corresponding carbocationic intermediates of the bromination process.

Comment

The stereospecific synthesis of 8-bromocamphor requires a preliminary bromination of 3,3-dibromocamphor to 3,3,8-tribromocamphor (Cachia, Darby, Eck & Money, 1976). The proposed mechanism of this reaction comprises a sequence of carbocationic intermediates of tertiary alcohol character (Dadson & Money, 1982). Recently, examination of the post-reaction mixture resulted in isolation of a minor product which, unlike the other products but similar to the cationic intermediates, bore a hydroxyl group. Its structure was assigned as 7,7-dibromo-3-dibromomethylene-2,2-dimethylnorbornan-1-ol on the basis of spectral data analysis (Antkowiak & Antkowiak, 1994a). The present paper reports the X-ray structure of this compound, (I), which confirms the proposed structure.

(I)

The six-membered ring adopts a slightly distorted boat conformation, while both five-membered rings have close to envelope conformations. The values of the asymmetry parameters (Duax & Norton, 1975) show similar distortions from the ideal geometry for all three rings. The C—O distance of $1.393\,(7)\,\text{Å}$ is shorter than the typical value of $1.440\,\text{Å}$ (Allen et al., 1987). The hydroxy group acts as a donor in the weak intermolecular $O1—H \cdots Br32(x - 1, y, z)$ hydrogen bond [$H \cdots Br\ 2.60\,(5)\,\text{Å}$, $O \cdots Br\ 3.167\,(5)\,\text{Å}$, $O—H \cdots Br\ 127\,(5)°$].

Both the position and hybridization of the atoms (except C31) in this molecule are very similar to those in the cationic intermediate from which it has been formed. Therefore, it is possible to use the X-ray data for estimating the steric relations and the non-bonding interactions in the carbocations which are subsequently formed during the functionalization of the camphor methyl groups in an acidic medium. The crowded part of the molecule, comprising the substituted C2, C3 and C7 atoms, seems to be particularly interesting. The distance of the C7-syn bromine to the C2-exo methyl and that to the sp^2-hybridized C3 are smaller than the sums of their van der Waals radii by about $0.5\,\text{Å}$ in both cases (Fig. 1). These observations strongly support the suggestion (Antkowiak & Antkowiak, 1994b) that the 3,2-endo methyl shift, which is unique for 3,3,8-tribromocamphor formation, results not only from steric hindrance but also from the participation of bromine non-bonding electrons in the formation of the transition state.
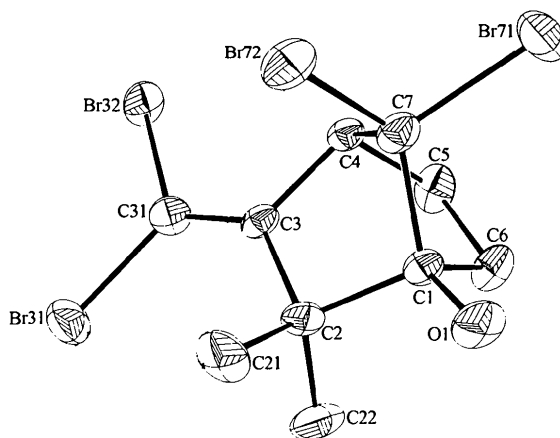
Fig. 1. View of the molecule with the labelling scheme. Some non-bonding distances (see text): $C21 \cdots Br31\ 3.497\,(9)$, $C21H \cdots Br31\ 2.83\,(1)$, $C22 \cdots Br31\ 3.466\,(11)$, $C22H \cdots Br31\ 2.77\,(1)$, $C21 \cdots Br72\ 3.283\,(11)$, $C21H \cdots Br72\ 2.52\,(1)$, $C3 \cdots Br72\ 3.168\,(7)\,\text{Å}$. The corresponding sums of van der Waals radii (Bondi, 1964) are: $Br \cdots C\ 3.7$, $Br \cdots H\ 3.0\,\text{Å}$. The displacement ellipsoids are drawn at the 33% probability level and H atoms are omitted for clarity.

Experimental

Crystal data

$C_{10}H_{12}Br_4O$	Cu $K\alpha$ radiation
$M_r = 467.84$	$\lambda = 1.5418\,\text{Å}$
Monoclinic	Cell parameters from 25
$P2_1$	reflections
$a = 8.8937\,(6)\,\text{Å}$	$\theta = 20.28–44.96°$
$b = 7.7404\,(6)\,\text{Å}$	$\mu = 14.675\,\text{mm}^{-1}$
$c = 9.5873\,(6)\,\text{Å}$	$T = 293\,(2)\,\text{K}$
$\beta = 91.528\,(9)°$	Prism
$V = 659.76\,(8)\,\text{Å}^3$	$0.45 \times 0.15 \times 0.15\,\text{mm}$
$Z = 2$	Colourless
$D_x = 2.355\,\text{Mg m}^{-3}$	Crystal source: CH_2Cl_2–n-hexane

Data collection

KM4 four-circle diffractometer	$R_{int} = 0.0309$
	$\theta_{max} = 75.09°$
$\omega/2\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction:	$k = 0 \rightarrow 8$
refined from ΔF	$l = 0 \rightarrow 12$
(DIFABS; Walker & Stuart, 1983)	3 standard reflections monitored every 100
1461 measured reflections	reflections
1385 independent reflections	intensity decay: 1.5%
1382 observed reflections	
$[I > 2\sigma(I)]$	

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.0329$	SHELXL93 (Sheldrick, 1993)
$wR(F^2) = 0.0909$	
$S = 1.094$	Extinction coefficient:
1385 reflections	0.0021 (3)

$C_{10}H_{12}Br_4O$

143 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0561P)^2 + 1.3243P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.630$ e Å^{-3}
$\Delta\rho_{min} = -0.596$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.6364 (7)	0.3522 (10)	0.1554 (7)	0.0308 (14)
O1	0.4859 (5)	0.3028 (10)	0.1441 (6)	0.0466 (13)
C2	0.7005 (7)	0.3373 (11)	0.3097 (7)	0.035 (2)
C21	0.6357 (10)	0.1801 (15)	0.3877 (10)	0.054 (2)
C22	0.6624 (10)	0.4988 (19)	0.3962 (11)	0.063 (3)
C3	0.8705 (6)	0.3267 (10)	0.2817 (7)	0.0308 (13)
C31	0.9860 (7)	0.3119 (13)	0.3739 (7)	0.040 (2)
Br31	0.96608 (10)	0.3036 (2)	0.56683 (8)	0.0582 (3)
Br32	1.18650 (7)	0.30281 (14)	0.31561 (9)	0.0502 (3)
C4	0.8892 (7)	0.3438 (9)	0.1258 (7)	0.0308 (14)
C5	0.8448 (9)	0.5362 (12)	0.0905 (9)	0.047 (2)
C6	0.6726 (8)	0.5325 (11)	0.0996 (9)	0.043 (2)
C7	0.7521 (8)	0.2458 (11)	0.0702 (8)	0.038 (2)
Br71	0.72005 (10)	0.2633 (2)	−0.13079 (8)	0.0569 (3)
Br72	0.76657 (10)	−0.00079 (12)	0.10599 (10)	0.0507 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—O1	1.393 (7)	C3—C4	1.515 (8)
C1—C6	1.532 (11)	C31—Br31	1.864 (7)
C1—C7	1.565 (9)	C31—Br32	1.884 (6)
C1—C2	1.575 (9)	C4—C7	1.521 (10)
C2—C22	1.543 (13)	C4—C5	1.575 (11)
C2—C3	1.544 (8)	C5—C6	1.537 (11)
C2—C21	1.547 (11)	C7—Br72	1.943 (9)
C3—C31	1.342 (9)	C7—Br71	1.945 (8)
O1—C1—C6	115.7 (6)	C3—C31—Br31	124.4 (5)
O1—C1—C7	117.3 (6)	C3—C31—Br32	121.5 (5)
C6—C1—C7	98.6 (5)	Br31—C31—Br32	114.1 (4)
O1—C1—C2	112.1 (5)	C3—C4—C7	101.2 (5)
C6—C1—C2	108.7 (6)	C3—C4—C5	105.1 (6)
C7—C1—C2	103.0 (5)	C7—C4—C5	101.7 (6)
C22—C2—C3	111.5 (6)	C6—C5—C4	102.4 (6)
C22—C2—C21	106.7 (7)	C1—C6—C5	104.8 (6)
C3—C2—C21	114.9 (7)	C4—C7—C1	95.0 (6)
C22—C2—C1	111.5 (7)	C4—C7—Br72	112.3 (5)
C3—C2—C1	99.9 (5)	C1—C7—Br72	117.8 (5)
C21—C2—C1	112.4 (6)	C4—C7—Br71	114.0 (5)
C31—C3—C4	123.7 (5)	C1—C7—Br71	113.5 (5)
C31—C3—C2	128.8 (6)	Br72—C7—Br71	104.5 (4)
C4—C3—C2	107.5 (5)		

Data collection: *KUMA KM4 Software* (Kuma Diffraction, 1991). Cell refinement: *KUMA KM4 Software*. Data reduction: *KUMA KM4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *Stereochemical Workstation* (Siemens, 1989). Software used to prepare material for publication: *SHELXL93*.

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1,4,7-Triazatricyclo[5.2.1.0⁴,¹⁰]decane at 100 K

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Abstract

Molecules of $C_7H_{13}N_3$ possess non-crystallographic C_3 symmetry. Their structure may be visualized as three five-membered CNCCN rings: each is in a twist conformation and shares edges with the other two rings and a common pivot C atom.

Comment

1,4,7-Triazatricyclo[5.2.1.0⁴·¹⁰]decane, (1), is a key intermediate in the synthesis of a range of N-substituted cyclononane ligands (Weisman, Vachon, Johnson & Gronbeck, 1987; Blake, Fallis, Parsons, Ross & Schröder, 1994). The homologous series of tricyclic trisaminomethanes has been the subject of a solution NMR study (Atkins, 1980), some of the conclusions from which are inconsistent with the results of the present crystal structure determination.