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1,7-Dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one

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$C_{10}H_{12}Br_4O$, orthorhombic, $P2_12_12_1$, $a = 10.270$ (2), $b = 26.614$ (7), $c = 9.881$ (3), Å, $d_x = 2.30$ g cm^{-3}, $Z = 8$, μ(Cu $K\alpha$) = 153.6 cm^{-1}. The norbornane skeleton is slightly twisted in both independent molecules with normal bond lengths and angles. The C–C–C bridge angles are 97 and 95° respectively.

Introduction

Small, colourless, well formed crystals were obtained by slow crystallization from a solution in diethyl ether. The density was measured as approximately 2 g cm^{-3} by flotation in aqueous thallous formate. Unit-cell and intensity data were measured on a Datex-automated G.E. XRD 6 diffractometer using Cu $K\alpha$ radiation and the θ–2θ scan technique. Unit-cell parameters were refined by least squares from the observed 2θ values of 17 reflexions. A standard reflexion monitored periodically throughout the data collection decreased in intensity by 21% and the data were accordingly scaled. Of the 2297 independent reflexions with $2\theta < 120°$, 1529 had intensities greater than $3\sigma(I)$ above background $[\sigma^2(I) = S + B + (0.04S)^2$, where S = scan and B = background count]. Lorentz and polarization corrections were applied and the structure amplitudes derived. Owing to the high value of the absorption coefficient and the crystal dimensions (0.016 × 0.019 × 0.022 cm) an absorption correction was applied by a computer program using a Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965; Busing & Levy, 1957).

The structure was solved by direct methods using symbolic addition and tangent refinement techniques. Origin-defining reflexions and starting symbols for this procedure were chosen manually. The eight Br atoms were located on the best E map and the solution proceeded by conventional Fourier methods. The non-hydrogen atoms were refined by the full-matrix least-squares procedure where the function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$, where $\sigma(F)$ values were derived from the previously calculated

$\sigma(I)$ values. All non-hydrogen atoms were included with anisotropic temperature factors and the scattering factors for Br were corrected for anomalous dispersion. H atoms were included in the structure-factor calculations with calculated geometry and fixed posi-

Table 1. *Final positional parameters (fractional* × 10^4*) with estimated standard deviations in parentheses*

	x	y	z
Br(1)	8807 (2)	7009 (1)	8365 (3)
Br(2)	6418 (3)	6855 (1)	10931 (3)
Br(3)	6059 (4)	7727 (1)	4291 (3)
Br(4)	7172 (3)	6661 (1)	4945 (3)
Br'(1)	9133 (3)	5500 (1)	5525 (3)
Br'(2)	6612 (3)	5559 (1)	8024 (3)
Br'(3)	13293 (3)	5050 (1)	8318 (4)
Br'(4)	12259 (3)	6087 (1)	7211 (4)
C(1)	6135 (25)	7168 (9)	9242 (23)
C(2)	6394 (27)	7723 (10)	9205 (31)
C(3)	6467 (24)	7889 (7)	7698 (30)
C(4)	6404 (23)	7357 (7)	6989 (23)
C(5)	4950 (24)	7161 (9)	7132 (31)
C(6)	4738 (24)	7093 (10)	8630 (27)
C(7)	6927 (22)	6984 (9)	8008 (23)
C(8)	5328 (25)	8248 (9)	7539 (33)
C(9)	7695 (27)	8188 (9)	7416 (27)
C(10)	6974 (24)	7317 (10)	5563 (26)
O	6550 (17)	7984 (7)	10153 (21)
C'(1)	8358 (22)	5367 (8)	8317 (25)
C'(2)	8573 (19)	4811 (10)	8124 (23)
C'(3)	10095 (21)	4724 (9)	8074 (28)
C'(4)	10570 (20)	5300 (7)	8094 (24)
C'(5)	10420 (25)	5522 (10)	9526 (23)
C'(6)	8887 (22)	5519 (10)	9758 (28)
C'(7)	9427 (25)	5590 (8)	7409 (28)
C'(8)	10456 (25)	4413 (10)	9287 (31)
C'(9)	10510 (23)	4421 (8)	6811 (26)
C'(10)	11928 (18)	5380 (10)	7421 (25)
O'	7807 (15)	4475 (6)	7988 (19)

Table 1 (cont.)

H(5a)	4782	6839	6590
H(5b)	4288	7420	6725
H(6a)	4488	7388	9203
H(6b)	4206	6791	8959
H(7)	6845	6613	7672
H(10)	7893	7470	5647
H(8a)	5512	8566	8081
H(8b)	5176	8345	6579
H(8c)	4504	8094	7920
H(9a)	7972	8397	8219
H(9b)	7618	8430	6611
H(9c)	8428	7951	7194
H'(5a)	10863	5306	10249
H'(5b)	10778	5871	9615
H'(6a)	8437	5820	10254
H'(6b)	8416	5208	10120
H'(7)	9519	5966	7439
H'(10)	11884	5203	6468
H'(8a)	11440	4424	9420
H'(8b)	10206	4051	9144
H'(8c)	10044	4529	10182
H'(9a)	11482	4366	6841
H'(9b)	10069	4085	6824
H'(9c)	10288	4598	5935

tional and thermal parameters. Atomic scattering factors for Br, O and C are those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). The real and imaginary parts of the anomalous scattering factors for Br were taken from Cromer & Liberman (1970). In the final stages of re-

finement extinction effects were apparent in the data and a correction was applied. A parameter E was introduced such that F_c was replaced in the calculations by F_{cor} where $F_{cor} = F_c/(1 + EI_0)$, I_0 being the uncorrected intensity (Stout & Jensen, 1968). The final value of E was 6.03×10^{-7}. The final R and R' ($= [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$) for the 1529 reflexions with $I > 3\sigma(I)$ are 0.060 and 0.064 respectively. The correct absolute configuration has been determined from comparison of the R values for the two enantiomorphs and it confirms that expected from the chemical preparation to better than 99.5% significance (Hamilton, 1965). For all 2297 data* R is 0.089 and R' is 0.065. The error in an observation of unit weight $\{[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}\}$ is 1.73. Final positional and thermal parameters are listed in Tables 1 and 2.

Discussion

Direct bromination of (+)-3,3-dibromocamphor gives a mixture of products including a tetrabromo derivative (Cachia, Darby, Eck & Money, 1976). The crystal structure analysis of this derivative

Table 2. Final thermal parameters and their estimated standard deviations ($U_{ij} \times 10^3$ $Å^2$)

Anisotropic thermal parameters in the expression

$$f = f^\circ \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$ U_{iso} for all H atoms is 6.3×10^{-2} $Å^2$.

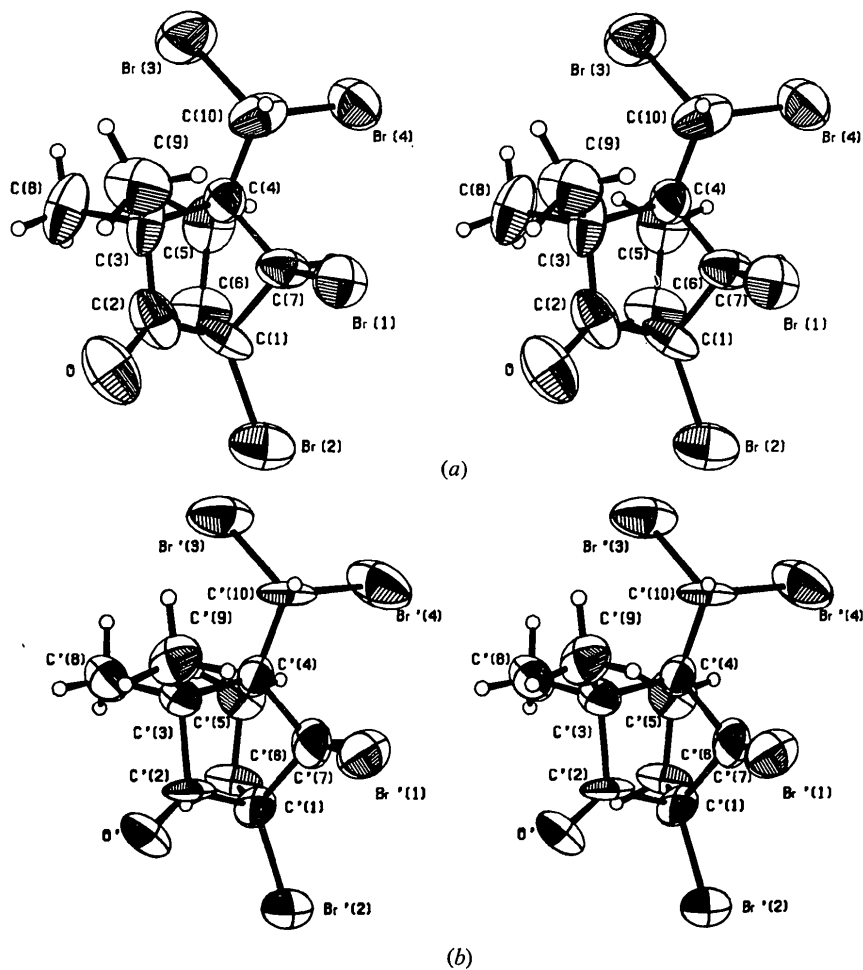|	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	52 (1)	88 (2)	67 (2)	2 (1)	−1 (1)	1 (2)
Br(2)	85 (2)	125 (3)	63 (2)	−16 (2)	12 (2)	6 (2)
Br(3)	105 (3)	129 (3)	80 (2)	20 (2)	−14 (2)	21 (2)
Br(4)	98 (2)	89 (2)	77 (2)	−1 (2)	12 (2)	−14 (2)
Br'(1)	66 (2)	94 (2)	67 (2)	16 (2)	−2 (2)	5 (2)
Br'(2)	49 (2)	39 (2)	107 (3)	5 (1)	7 (2)	8 (2)
Br'(4)	85 (2)	89 (2)	171 (4)	−35 (2)	39 (3)	−26 (2)
Br'(3)	46 (2)	177 (3)	97 (2)	6 (2)	−8 (2)	6 (3)
C(1)	63 (17)	105 (21)	46 (15)	−10 (15)	23 (13)	−23 (14)
C(2)	65 (18)	78 (19)	79 (21)	−3 (15)	−17 (16)	−42 (17)
C(3)	48 (15)	42 (13)	120 (25)	10 (11)	−1 (16)	1 (14)
C(4)	58 (15)	50 (13)	62 (16)	−4 (11)	7 (14)	−1 (12)
C(5)	47 (15)	90 (18)	106 (24)	−9 (13)	−37 (16)	−11 (17)
C(6)	55 (16)	107 (20)	61 (18)	−47 (15)	2 (14)	1 (16)
C(7)	56 (16)	101 (18)	41 (14)	6 (14)	−8 (12)	0 (15)
C(8)	75 (18)	60 (15)	141 (28)	17 (14)	−19 (20)	11 (18)
C(9)	93 (21)	87 (18)	79 (20)	−33 (16)	5 (17)	−4 (15)
C(10)	51 (16)	102 (19)	75 (19)	−8 (14)	−2 (14)	35 (16)
O	69 (12)	100 (13)	105 (16)	−14 (11)	12 (12)	−40 (13)
C'(1)	59 (15)	61 (14)	64 (17)	32 (12)	27 (16)	6 (14)
C'(2)	19 (12)	112 (20)	49 (15)	11 (13)	6 (12)	12 (15)
C'(3)	47 (14)	82 (17)	72 (19)	5 (12)	15 (15)	29 (16)
C'(4)	53 (14)	45 (13)	57 (16)	3 (11)	−5 (13)	6 (12)
C'(5)	85 (19)	100 (18)	31 (13)	−7 (17)	−7 (13)	−9 (14)
C'(6)	40 (14)	105 (19)	86 (20)	−7 (15)	15 (14)	−20 (17)
C'(7)	85 (20)	40 (13)	111 (22)	18 (13)	36 (18)	14 (15)
C'(8)	60 (18)	95 (19)	108 (24)	−18 (16)	−4 (17)	40 (19)
C'(9)	69 (17)	55 (14)	77 (18)	9 (13)	1 (16)	−18 (15)
C'(10)	21 (12)	113 (19)	74 (19)	5 (12)	3 (12)	−15 (15)
O'	55 (10)	70 (10)	110 (15)	−30 (9)	6 (11)	7 (11)

(a)

(b)

Fig. 1. (a) Stereo diagram of 1,7-dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one, molecule 1, showing the absolute configuration. (b) Stereo diagram of 1,7-dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one, molecule 2.
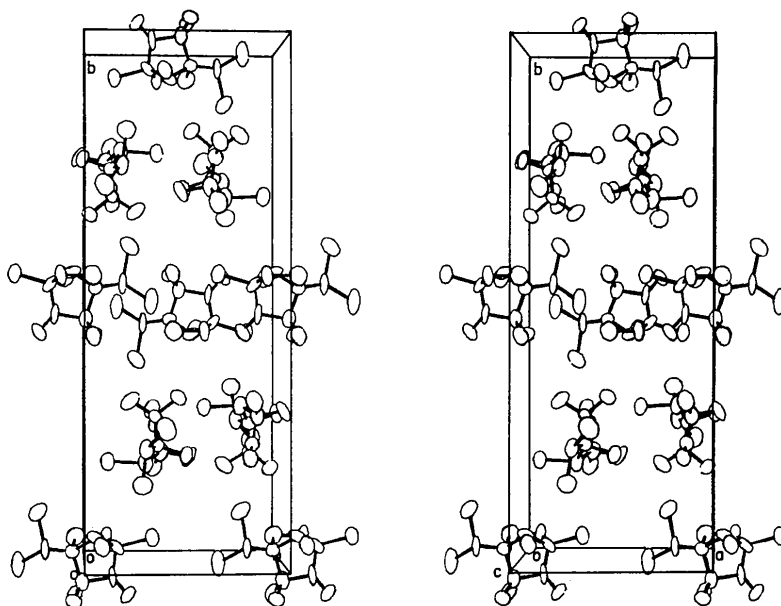

Fig. 2. Stereo diagram of the contents of the unit cell.

Table 3. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

(a) Bond distances

	Molecule 1	Molecule 2
Br(1)–C(7)	1·96 (2)	1·90 (2)
Br(2)–C(1)	1·89 (3)	1·89 (2)
Br(3)–C(10)	1·91 (2)	1·88 (2)
Br(4)–C(10)	1·86 (3)	1·92 (3)
C(1) –C(2)	1·50 (3)	1·51 (3)
C(1) –C(6)	1·57 (3)	1·58 (3)
C(1) –C(7)	1·54 (3)	1·54 (3)
C(2) –O	1·18 (3)	1·20 (2)
C(2) –C(3)	1·56 (4)	1·58 (3)
C(3) –C(4)	1·58 (3)	1·61 (3)
C(3) –C(8)	1·52 (3)	1·50 (3)
C(3) –C(9)	1·52 (3)	1·55 (3)
C(4) –C(5)	1·59 (3)	1·54 (3)
C(4) –C(7)	1·51 (3)	1·56 (3)
C(4) –C(10)	1·53 (3)	1·56 (3)
C(5) –C(6)	1·51 (4)	1·59 (3)

(b) Bond angles

	Molecule 1	Molecule 2
Br(2)–C(1)—C(2)	115 (2)	113 (2)
Br(2)–C(1)—C(6)	115 (2)	113 (1)
Br(2)–C(1)—C(7)	118 (2)	119 (2)
C(2) –C(1)—C(6)	106 (2)	108 (2)
C(2) –C(1)—C(7)	101 (2)	102 (2)
C(6) –C(1)—C(7)	98 (2)	101 (2)
C(1) –C(2)—O	126 (3)	131 (2)
C(1) –C(2)—C(3)	108 (2)	107 (2)
C(3) –C(2)—O	126 (2)	122 (2)
C(2) –C(3)—C(4)	100 (2)	99 (2)
C(2) –C(3)—C(8)	104 (2)	107 (2)
C(2) –C(3)—C(9)	111 (2)	112 (2)
C(4) –C(3)—C(8)	119 (2)	116 (2)
C(4) –C(3)—C(9)	115 (2)	115 (2)
C(8) –C(3)—C(9)	107 (2)	107 (2)
C(3) –C(4)—C(5)	107 (2)	110 (2)
C(3) –C(4)—C(7)	106 (2)	104 (2)
C(3) –C(4)—C(10)	117 (2)	113 (2)
C(5) –C(4)—C(7)	93 (2)	98 (2)
C(5) –C(4)—C(10)	115 (2)	115 (2)
C(7) –C(4)—C(10)	116 (2)	115 (2)
C(4) –C(5)—C(6)	105 (2)	103 (2)
C(5) –C(6)—C(1)	103 (2)	102 (2)
Br(1)–C(7)—C(1)	111 (2)	114 (2)
Br(1)–C(7)—C(4)	116 (2)	119 (2)
C(1) –C(7)—C(4)	97 (2)	95 (2)
Br(3)–C(10)–Br(4)	112 (1)	112 (1)
Br(3)–C(10)–C(4)	112 (2)	114 (1)
Br(4)–C(10)–C(4)	114 (1)	110 (2)

was undertaken in order to confirm that it was 1,7-dibromo-4-dibromomethyl-3,3-dimethylnorbornan-2-one as expected from the chemical evidence.

Stereo diagrams of the two independent molecules are shown in Fig. 1(a) and (b) respectively. Corresponding bond lengths and angles (see Table 3) in the two molecules are not significantly different and the mean C–Br bond distance is 1·90 (1) Å. The norbornane skeleton is slightly twisted in a similar way to that in the corresponding dibromo molecule, 3,3,4-trimethyl-1,7-dibromonorbornan-2-one (Bear & Trotter, 1975a). The angles between the C(1), C(4), C(7) plane and the four-atom planes of the six-membered ring [C(1), C(2), C(3), C(4) and C(1), C(4), C(5), C(6)] are 132 and 117° for molecule 1 and 127 and 120° for molecule 2, compared with 127·1 and 119·1° for the dibromo compound. The skeletons of the related molecules (+)-8-bromocamphor (Bear & Trotter, 1975b) and 3,9,9-tribromocamphor (Rendle & Trotter, 1975) are rather more symmetrical. Bond lengths and angles closely follow the trends shown by 3,3,4-trimethyl-1,7-dibromonorbornan-2-one but subtle differences may be hidden by the low accuracy of the C atom positional parameters. The C(7) bridgehead angles of 97 (2) and 95 (2)° are close to those of all three related molecules.

A stereo diagram of the packing arrangement in the unit cell is shown in Fig. 2. Alternate layers, of molecules 1 and 2 respectively, lie perpendicular to the crystallographic *b* axis. The two symmetry-independent layers have similar internal arrangements oriented at 90° to one another within the *ac* plane. This accounts for the near equivalence of the *a* and *c* axes. Intermolecular distances correspond to van der Waals interactions and there is no evidence of the C–H···O interactions observed in 3,9,9-tribromocamphor.

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