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References

Chu, S. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* **15**, 661–671.

Declerq, J. P., Germain, G., Main, P. & Woolfson, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Trotter, J. (1960). *Acta Cryst.* **13**, 86–95.

Yates, P., Ardao, M. I. & Fieser, L. P. (1956). *J. Amer. Chem. Soc.* **78**, 650–656.

Acta Cryst. (1975). B**31**, 2512

3,9,9-Tribromocamphor

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Abstract. $C_{10}H_{13}Br_3O$, monoclinic, $P2_1$, $a=8{\cdot}949$ (5), $b=7{\cdot}712$ (7), $c=8{\cdot}996$ (9) Å, $\beta=93{\cdot}33$ (5)°, $Z=2$, $D_x=2{\cdot}08$ g cm^{-3}, μ(Mo $K\alpha$) = 102·8 cm^{-1}. The norbornane skeleton is undistorted, with close to normal bond lengths and angles. The C–C–C bridge angle is 95°. The molecules are linked by C–H···O hydrogen bonds in the solid state.

Introduction. The colourless crystals were small and poorly formed. Unit-cell and intensity data were measured on a Datex-automated G. E. XRD 6 diffractometer with Mo $K\alpha$ radiation and the θ–2θ scan technique. A standard reflexion monitored periodically throughout data collection decreased in intensity by 40% and the data were accordingly scaled. Of 1181 independent reflexions with $2\theta \le 50°$, 507 had intensities greater than 2σ above background [$\sigma^2(I)=S+B+(0{\cdot}09S)^2$, where $S=$ scan and $B=$ background count]. Absorption corrections were not made in view of the irregular crystal surface. The structure was solved by Patterson and Fourier syntheses. Refinement was by full-matrix least-squares techniques in which the function minimized was $\sum w(F_o-F_c)^2$ with weights w derived from counting statistics. The scattering factors for bromine were corrected for the real and imaginary parts of anomalous dispersion, and each bromine was refined with anisotropic thermal parameters. An attempt to refine all atoms with anisotropic thermal parameters resulted in non-positive-definite tensors for two of the carbon atoms and so the light atoms were refined with isotropic thermal parameters. Hydrogen atoms were included in the structure-factor calculations with fixed positional and thermal parameters. The correct absolute configuration has been determined (it is in any case determined from the chemical preparation), and the final R and R' $(=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2})$ for the 507 reflexions with $I \ge 2\sigma(I)$ are 0·066 and 0·076 [the opposite enantiomorph has $R=0{\cdot}067$ and $R'=0{\cdot}078$, and hence may be rejected at the 0·5% significance level (Hamilton, 1965)]. Three low-angle reflexions 020, 040, and 021 were given zero weight in the last two cycles of refinement because of suspected extinction effects. For all 1181 data R was 0·148 and R' 0·088.*

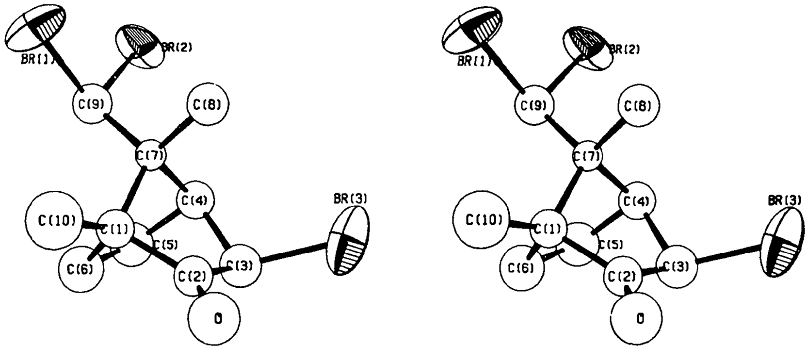

Fig. 1. Stereo diagram of 3,9,9-tribromocamphor showing the absolute configuration of the molecule.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31169 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters, all with estimated standard deviations in parentheses*

(*a*) Final positional parameters (fractional $\times 10^4$)

	x/a	y/b	z/c
Br(1)	1324 (5)	1735 (9)	4742 (5)
Br(2)	−1051 (4)	0	2478 (5)
Br(3)	2990 (5)	−374 (8)	−1873 (4)
O	5598 (26)	−592 (31)	752 (24)
C(1)	3658 (33)	−921 (42)	2556 (34)
C(2)	4335 (35)	−998 (37)	1045 (33)
C(3)	3158 (36)	−1681 (46)	−38 (35)
C(4)	1733 (32)	−1534 (41)	900 (33)
C(5)	1898 (40)	−3183 (54)	1886 (38)
C(6)	3217 (40)	−2831 (49)	2911 (40)
C(7)	2143 (27)	−142 (38)	2092 (27)
C(8)	2267 (35)	1700 (47)	1375 (34)
C(9)	1009 (33)	−170 (45)	3315 (32)
C(10)	4626 (44)	−33 (64)	3770 (43)
H(3)	3339	−2996	−425
H(4)	765	−1384	349
H(5*a*)	2034	−4256	1221
H(5*b*)	923	−3408	2403
H(6*a*)	4036	−3676	2775
H(6*b*)	2918	−2916	3991
H(8*a*)	2980	1587	510
H(8*b*)	1275	2057	931
H(8*c*)	2685	2511	2101
H(9)	1166	−1258	3870
H(10*a*)	4147	86	4733
H(10*b*)	5643	−672	4002
H(10*c*)	4934	1181	3434

(*b*) Anisotropic thermal parameters ($U_{ij} \times 10^3$ Å^2)

The anisotropic temperature factor expression is of the form:

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	80 (3)	104 (4)	88 (3)	9 (3)	38 (3)	−34 (3)
Br(2)	30 (2)	103 (3)	105 (3)	24 (2)	21 (2)	43 (3)
Br(3)	115 (4)	110 (4)	56 (3)	−45 (3)	27 (3)	−2 (3)

(*c*) Isotropic thermal parameters ($U \times 100$)

	U (Å^2)		U (Å^2)
O	6·9 (7)	C(6)	6·6 (10)
C(1)	4·2 (8)	C(7)	2·9 (6)
C(2)	4·3 (8)	C(8)	5·1 (9)
C(3)	5·6 (9)	C(9)	5·2 (8)
C(4)	4·8 (9)	C(10)	8·7 (12)
C(5)	6·8 (10)	H	6·3

Table 2. *Bond lengths* (Å) *and valency angles* (°) *with estimated standard deviations in parentheses*

(*a*) Bond distances

Br(1)–C(9)	1·96 (3)	C(2)–C(3)	1·49 (4)
Br(2)–C(9)	1·96 (3)	C(3)–C(4)	1·57 (4)
Br(3)–C(3)	1·93 (3)	C(4)–C(5)	1·55 (5)
O——C(2)	1·22 (3)	C(4)–C(7)	1·55 (4)
C(1) –C(2)	1·52 (4)	C(5)–C(6)	1·48 (5)
C(1) –C(6)	1·56 (5)	C(7)–C(8)	1·57 (4)
C(1) –C(7)	1·52 (4)	C(7)–C(9)	1·54 (4)
C(1) –C(10)	1·52 (5)		

(*b*) Valency angles

C(2)–C(1)–C(6)	105 (3)	C(3) –C(4)–C(7)	105 (2)
C(2)–C(1)–C(7)	99 (2)	C(5) –C(4)–C(7)	99 (2)
C(2)–C(1)–C(10)	115 (3)	C(4) –C(5)–C(6)	105 (3)
C(6)–C(1)–C(7)	101 (2)	C(1) –C(6)–C(5)	104 (3)
C(6)–C(1)–C(10)	115 (3)	C(1) –C(7)–C(4)	95 (2)
C(7)–C(1)–C(10)	119 (3)	C(1) –C(7)–C(8)	113 (2)
O——C(2)–C(1)	127 (3)	C(1) –C(7)–C(9)	114 (2)
O——C(2)–C(3)	125 (3)	C(4) –C(7)–C(8)	111 (2)
C(1)–C(2)–C(3)	107 (3)	C(4) –C(7)–C(9)	110 (2)
C(2)–C(3)–C(4)	101 (3)	C(8) –C(7)–C(9)	112 (2)
C(2)–C(3)–Br(3)	113 (2)	Br(1)–C(9)–C(7)	112 (2)
C(4)–C(3)–Br(3)	113 (2)	Br(2)–C(9)–C(7)	112 (2)
C(3)–C(4)–C(5)	101 (2)	Br(1)–C(9)–Br(2)	107 (2)

The error in an observation of unit weight ($[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$) was 0·92, which suggests that the 0·09 factor in the expression for the variance is too high. Final positional and thermal parameters are listed in Table 1, and bond lengths and valency angles in Table 2.

Discussion. The crystal structure analysis was undertaken to assist in the characterization of a by-product in the preparation of 3,9-dibromocamphor (Cachia, Darby, Eck & Money, 1975). The byproduct has been confirmed as 3,9,9-tribromocamphor.

Fig. 1 is a stereo diagram of the molecule (hydrogen atoms omitted) in the correct absolute configuration. The presence of three bromine atoms appears to cause little distortion in the norbornane skeleton. The six-membered ring is a fairly symmetrical boat with atoms C(1) and C(4) displaced 0·80 (3) and 0·95 (3) Å above the best plane through atoms C(2), C(3), C(5), and C(6). The bridgehead angle is 95 (2)° and the remainder

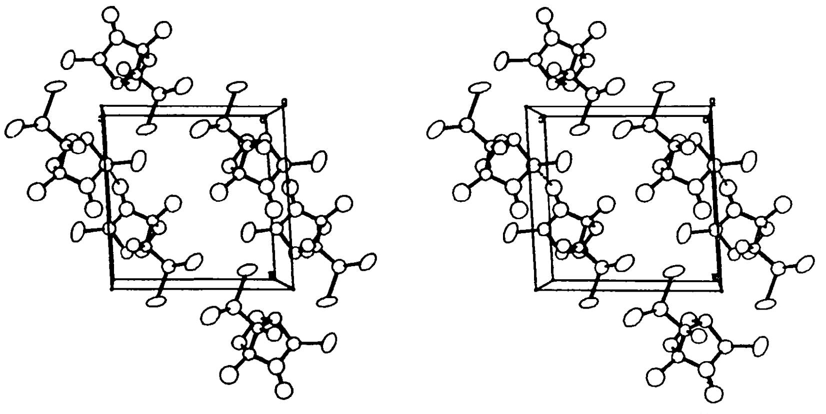

Fig. 2. Stereo diagram of the contents of the unit cell.

of the endocyclic valency angles follow the same trend as those in (+)-8-bromocamphor (Bear & Trotter, 1975*a*) rather than, for example, those in (−)-3,3,4-trimethyl-1,7-dibromonorbornan-2-one, a structure with a slightly twisted norbornane skeleton (Bear & Trotter, 1975*b*). The accuracy with which the positions of the carbon atoms are known is low and hence subtle differences in C–C bond lengths may be hidden. The $C(sp^3)$–$C(sp^2)$ distances C(1)–C(2) and C(2)–C(3) are 1·52 (4) and 1·49 (4) Å. The angles between the C(1), C(4), C(7) plane and the four-atom planes of the six-membered boat [C(1), C(2), C(3), C(4), and C(1), C(4), C(5), C(6)] are 127·6 and 124·0°, comparing reasonably well with the corresponding dihedral angles of 124·5 and 124·2° in (+)-8-bromocamphor. The C–Br distances average 1·95 (1) Å.

Fig. 2 is a stereo diagram of the contents of the unit cell. The molecules are linked into infinite chains about the twofold screw axes by C(3)–H···O interactions (broken line in Fig. 2), which may represent hydrogen bonds. Br(3), by way of the inductive effect, presumably causes H(3) to be quite acidic. The C(3)···O distance is 3·29 Å; with H(3) in its calculated position, the H···O distance is about 2·3 Å, and the C–H···O angle is about 160°. These parameters are in agreement with those in other documented C–H···O hydrogen bonds *e.g.* O···H 2·27 Å and C–H···O 164° in 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)-hydrazine monohydrate (Palenik, 1965). The intramolecular nonbonded Br(1)···Br(2) distance is 3·156 (7) Å, and the only other intermolecular contacts of < 3·5 Å are O···Br(2) $[1+x,y,z]$ 3·33 (2) Å and O···C (8) $[1-x,y-\frac{1}{2},-z]$ 3·48 (4) Å.

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References

Bear, C. A. & Trotter, J. (1975*a*). *Acta Cryst.* **B31**, 903.
Bear, C. A. & Trotter, J. (1975*b*). *Acta Cryst.* **B31**, 904.
Cachia, P., Darby, N., Eck, C. R. & Money, T. (1975). *J. Chem. Soc. Perkin* I. In the press.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
Palenik, G. J. (1965). *Acta Cryst.* **19**, 47–56.

Acta Cryst. (1975). **B31**, 2514

Chloro-α,β,γ,δ-tetraphenylporphinatopyridinecobalt(III)

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Abstract. $C_{49}H_{33}N_5CoCl.\frac{1}{2}(C_6H_6)$, monoclinic, $P2_1/n$, $a=14\cdot50\,(4)$, $b=23\cdot42\,(6)$, $c=13\cdot12\,(3)$ Å, $\beta=102\cdot1\,(3)°$, $V=4357\,(19)$ Å^3; $D_x=1\cdot258$ g cm^{-3}. $R=7\cdot3\,\%$, 3997 observed reflexions. The cobalt atom is in the plane of the four pyrrole nitrogen atoms and has nearly exact octahedral coordination. The porphinato core is considerably ruffled. The overall symmetry of the tetraphenyl porphinato group is $\bar{4}$.

Introduction. Several six-coordinate cobalt(III) complexes of α,β,γ,δ-tetraphenylporphyrin (TPP) have been prepared in our Institute (Yamamoto & Tonomura, 1964). The effects of axial ligands on the complexes were studied by electronic absorption and nuclear magnetic resonance spectra. The title compound [ClTPP.PyCo^{III}] was chosen to determine the three-dimensional structure. The complex was obtained by heating Co^{II}TPP with pyridine in a hydrochloric acidic benzene–methanol mixture. The violet metallic-lustrous prismatic crystals were identified by elemental analysis. Found: C 75·80, H 4·28, N 8·56, Co 7·18, Cl 4·25 %. Calculated: C 75·71, H 4·36, N 8·49, Co 7·14, Cl 4·30 %, for $C_{52}H_{36}N_5CoCl$ [ClTPP.PyCo.$\frac{1}{2}(C_6H_6)$].

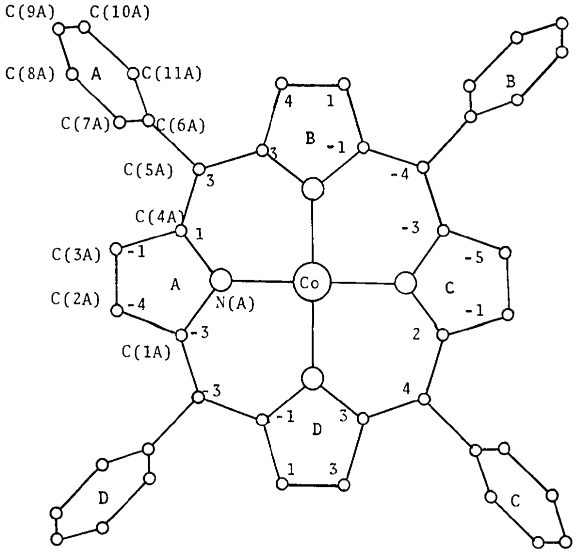

Fig. 1. The numbering scheme for the atoms used in this paper. The numerals attached to the atoms in the porphinato core represent perpendicular displacements from the mean plane in units of 0·1 Å.