Crystal and Molecular Structure of 15-Bromolongibornane-8,9-dione †

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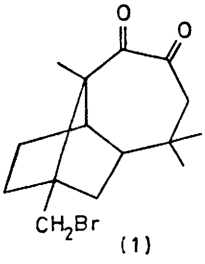
The crystal and molecular structure of the title compound (1) has been determined by the heavy-atom method from 1038 observed three-dimensional photographic data. Crystals are orthorhombic, with a = 20.07 ± 0.02, b = 10.05 ±0.02, c = 7.31 ± 0.01 Å, space group $P2_12_12_1$, with Z = 4. The structure was refined by block-diagonal least-squares to R 0.099. The conformation of the norbornane moiety is discussed. The seven-membered ring portion of the molecule adopts an approximate chair conformation. The packing of the molecules in the crystal is mainly a consequence of van der Waals interactions.

WHILE studying the acid rearrangement of a bromo-derivative of the sesquiterpene longifolene a novel rearrangement product was obtained.[1] On the basis of spectral evidences (i.r. and n.m.r.) a number of structures were suggested. An unambiguous determination of the structure by X-ray crystallography was considered important as the rearrangement path for the compound was expected to have interesting mechanistic implications. Further the determination of the structure as (1) provided additional information regarding the geometry of the norbornane system.



(1)

EXPERIMENTAL

Crystal Data.—$C_{15}H_{21}O_2Br$, $M = 313$. Orthorhombic, $a = 20.07 \pm 0.02$, $b = 10.05 \pm 0.02$, $c = 7.31 \pm 0.01$ Å, D_m (by flotation) $= 1.41$ g cm^{-3}, $Z = 4$, $D_c = 1.43$ g cm^{-3}. Space group $P2_12_12_1(D_2^4$, No. 19), from systematic absences. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) $= 41.9$ cm^{-1}.

Unit-cell data were obtained from rotation and Weissenberg photographs taken with Cu-K_α radiation. Three-dimensional intensity data were collected by use of Cu-K_α radiation for the layers hk0—6 with rotation along the c axis. As the crystal was brittle, it was not possible to cut one suitable for data collection about another axis. Intensities were measured visually and corrected for Lorentz, polarization, and spot-shape factors.[2] An approximate correction for absorption [3] was made by assuming the crystal to be cylindrical (μr 1.00). Of 1 281 reflections possible within the region surveyed, 1 038 were measured, and placed on an approximate layer scale by Wilson plots.[4]

Structure Determination and Refinement.—A three-dimensional Patterson map enabled location of the bromine atom, and a Fourier map, phased on this revealed the remaining

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† Systematic name 1-bromomethyl-2,6,6-trimethyltricyclo-[5.3.1.$0^{2,8}$]undecane-3,4-dione.

[1] G. Mehta and S. K. Kapoor, *Tetrahedron Letters*, 1972, 715.

[2] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[3] J. H. Palm, *Acta Cryst.*, 1964, **17**, 1326.

[4] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

non-hydrogen atom positions. Positional parameters, individual isotropic temperature parameters, and individual layer scale-factors were then refined.[5] The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight of an observation. The distribution of $|\Delta F|^2$ *vs.* $|F_o|$ suggested a weighting scheme[6] of the form $w = 1/F_{\text{min.}}$ for $|F_o| \leqslant |F_{\text{min.}}|$ and $w = 1\ |F_o|$ for $|F_o| > |F_{\text{min.}}|$ with $F_{\text{min.}}$ 3.6. A three-dimensional difference electron-density map computed at this stage (R 0.136) showed peaks ranging from 0.3 to 0.7 eÅ^{-3} at sites where hydrogen atoms were expected to be. Three cycles of refinement with anisotropic temperature factors for all non-hydrogen atoms and refining the overall scale-factor, gave R 0.099 for all observed 1 038 reflections. Hydrogen atoms were included in calculated positions (assuming C–H 1.0 Å). The shifts in the parameters after the last cycle were $< 0.1\ \sigma$. In all structure-factor calculations, atom scattering factors for carbon, oxygen, and bromine were taken from ref. 7, and for hydrogen from ref. 8, those for bromine being corrected for the real part of anomalous dispersion ($\Delta f'$).[9]

Final positional and thermal parameters for non-hydrogen atoms are recorded in Table 1. Observed and calculated structure-factors, calculated hydrogen atom positions, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21313 (9 pp., 1 microfiche).*

TABLE 1

Positional co-ordinates (× 10^4), with standard deviations in parentheses, of all non-hydrogen atoms

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Br	4 397(1)	−2 150(1)	7 044(3)
C(1)	4 005(5)	2 461(9)	5 099(18)
C(2)	3 946(6)	1 068(11)	6 111(22)
C(3)	4 086(6)	60(12)	4 637(18)
C(4)	4 856(7)	217(11)	4 129(21)
C(5)	4 864(7)	1 588(13)	2 970(23)
C(6)	4 112(6)	2 083(12)	3 118(21)
C(7)	3 743(5)	707(10)	2 932(19)
C(8)	2 998(7)	837(12)	3 183(21)
C(9)	2 679(6)	2 242(11)	3 346(20)
C(10)	2 697(7)	2 968(15)	5 058(24)
C(11)	3 426(6)	3 521(11)	5 513(21)
C(12)	3 450(11)	3 829(24)	7 531(24)
C(13)	3 537(9)	4 821(13)	4 385(29)
C(14)	3 830(8)	−92(14)	1 046(23)
C(15)	3 885(7)	−1 377(10)	5 073(17)
O(1)	2 610(4)	−133(9)	3 268(16)
O(2)	2 498(7)	2 816(12)	1 937(21)

DISCUSSION

Description of the Structure.—The *X*-ray investigations showed the structure to have the structure (1) as shown in Figure 1. Bond lengths and angles and their standard derivations are recorded in Table (2). The C–Br distance (1.952 Å) is in good agreement with the usual value for a C(sp^3)–Br bond.[10] The mean C–C bond length within the bicyclic moiety (1.569 ± 0.018 Å) compares well with the value observed in other structures containing this system.[11,12] Electron diffraction studies[13] on a substituted norbornane system show a mean bond length of 1.550 ± 0.015 Å. However in the present structure the C(1)–C(6) and C(2)–C(3) bond lengths are equal, mean 1.508 Å, which is much shorter than the other C–C bonds in the norbornane system. All internal angles in the norbornane system are less than the tetrahedral value (109.5°), the apex angle C(3)–C(7)–C(6) being as small as 95.1 (9)°. These features are consistent with the situation observed from *X*-ray investigations of other norbornanes as well as with the values obtained *via* molecular mechanics calculations.[14,15] In the seven-membered ring all internal angles at sp^3 hybridized carbon atoms, with the exception of C(1)–C(6)–C(7), are larger than the tetrahedral value, mean 113.6(8)°, but the value at the sp^2 hybridized carbon atoms C(8) and C(9) is not different from the expected 120°. No significance can be attached to the variations in the C(sp^3)–C(sp^3) bonds in the seven-membered ring, especially since the thermal vibrations of the atoms of this ring are much greater than those of the

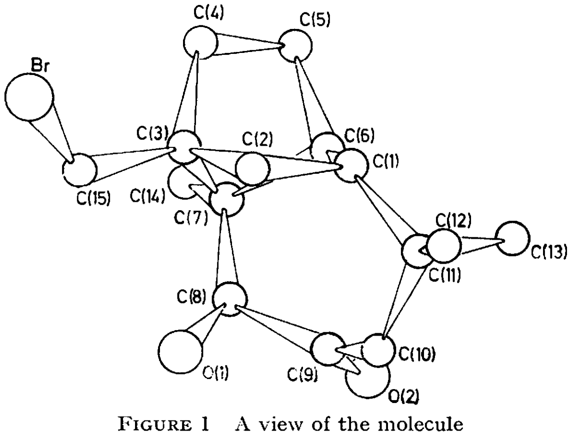

FIGURE 1 A view of the molecule

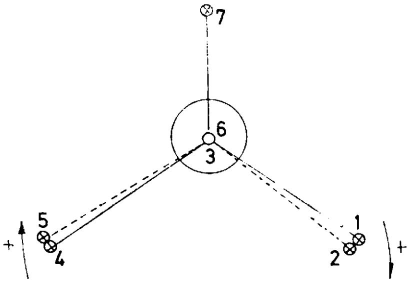

FIGURE 2 Newman projection down the C(3) · · · C(6) vector

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[5] R. Shiono, 1968, refinement program, personal communication.

[6] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

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[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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[10] *Chem. Soc. Special Publ.*, No. 18, 1965.

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[12] A. F. Cesur and D. F. Grant, *Acta Cryst.*, 1965, **18**, 55.

[13] J. F. Chiang, C. F. Wilcox, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1968, **90**, 3149.

[14] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.

[15] E. M. Engler, J. D. Andose, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

norbornane system. The C(8)–0(1) and C(9)–O(2) bond distances (1.250 and 1.235 Å) are in agreement with the value (1.25 Å) observed in carboxylate ions.[16]

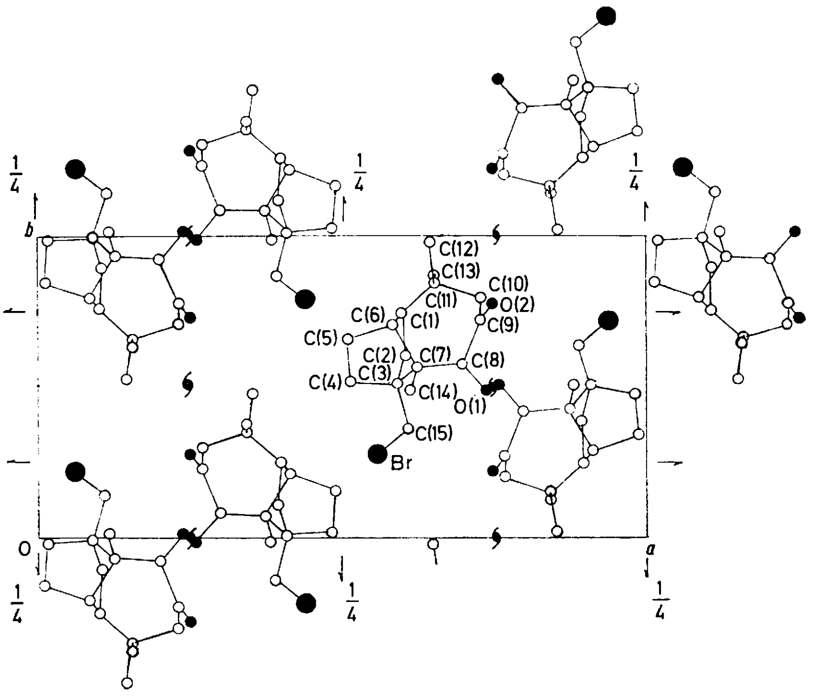

FIGURE 3 Molecular packing viewed down the *c* axis

Conformation of the Molecule.—Table 3 records the torsion angles about various single bonds in the molecule. The torsion angles within the norbornane moiety compare well with values obtained in ref. 14 from theoretical calculations.[14] The difference between the torsion angles

TABLE 2

(*a*) Bond lengths (Å)

C(1)–C(2)	1.587(17)	C(7)–C(8)	1.512(18)
C(1)–C(6)	1.512(20)	C(7)–C(14)	1.604(20)
C(1)–C(11)	1.605(16)	C(8)–C(9)	1.555(17)
C(2)–C(3)	1.505(19)	C(8)–O(1)	1.250(15)
C(3)–C(4)	1.598(17)	C(9)–C(10)	1.449(22)
C(3)–C(7)	1.565(18)	C(9)–O(2)	1.235(20)
C(3)–C(15)	1.527(16)	C(10)–C(11)	1.601(20)
C(4)–C(5)	1.617(19)	C(11)–C(12)	1.508(23)
C(5)–C(6)	1.592(18)	C(11)–C(13)	1.560(20)
C(6)–C(7)	1.574(16)	C(15)–Br	1.952(12)

(*b*) Bond angles (°)

C(1)–C(2)–C(3)	104.3(1.0)	C(7)–C(8)–C(9)	119.7(1.1)
C(2)–C(3)–C(4)	106.3(1.0)	C(7)–C(8)–O(1)	123.7(1.2)
C(2)–C(3)–C(7)	102.0(1.0)	O(1)–C(8)–C(9)	116.6(1.2)
C(2)–C(3)–C(15)	116.7(1.0)	C(8)–C(9)–C(10)	120.9(1.2)
C(4)–C(3)–C(7)	101.5(0.9)	C(8)–C(9)–O(2)	118.8(1.2)
C(4)–C(3)–C(15)	113.2(1.0)	O(2)–C(9)–C(10)	119.4(1.3)
C(7)–C(3)–C(15)	115.4(1.0)	C(9)–C(10)–C(11)	112.2(1.2)
C(3)–C(4)–C(5)	102.4(1.0)	C(10)–C(11)–C(12)	107.7(1.3)
C(4)–C(5)–C(6)	102.8(1.1)	C(10)–C(11)–C(13)	108.2(1.2)
C(5)–C(6)–C(1)	106.2(1.0)	C(10)–C(11)–C(1)	113.8(1.1)
C(5)–C(6)–C(7)	99.5(1.0)	C(12)–C(11)–C(1)	107.3(1.2)
C(1)–C(6)–C(7)	103.7(1.0)	C(13)–C(11)–C(1)	110.7(1.1)
C(6)–C(7)–C(3)	95.1(0.9)	C(12)–C(11)–C(13)	109.9(1.3)
C(6)–C(7)–C(8)	112.2(1.0)	C(11)–C(1)–C(2)	116.4(1.0)
C(6)–C(7)–C(14)	117.6(1.0)	C(11)–C(1)–C(6)	116.7(1.0)
C(3)–C(7)–C(8)	112.0(1.0)	C(2)–C(1)–C(6)	103.6(1.0)
C(3)–C(7)–C(14)	115.3(1.0)	C(3)–C(15)–Br	112.4(0.8)
C(8)–C(7)–C(14)	104.8(1.0)		

TABLE 3

Torsion angles (°)

C(6)–C(1)–C(2)–C(3)	4.9(1.2)
C(11)–C(1)–C(2)–C(3)	134.4(1.1)
C(1)–C(2)–C(3)–C(4)	68.8(1.1)
C(1)–C(2)–C(3)–C(7)	−37.2(1.1)
C(1)–C(2)–C(3)–C(15)	−163.9(1.0)
C(2)–C(3)–C(4)–C(5)	−74.1(1.2)
C(15)–C(3)–C(4)–C(5)	156.5(1.0)
C(7)–C(3)–C(4)–C(5)	32.2(1.1)
C(3)–C(4)–C(5)–C(6)	4.5(1.2)
C(4)–C(5)–C(6)–C(7)	−39.3(1.2)
C(4)–C(5)–C(6)–C(1)	68.0(1.2)
C(5)–C(6)–C(7)–C(8)	175.2(1.0)
C(5)–C(6)–C(7)–C(3)	58.9(1.0)
C(5)–C(6)–C(7)–C(14)	−63.2(1.3)
C(1)–C(6)–C(7)–C(8)	65.9(1.2)
C(1)–C(6)–C(7)–C(14)	−172.5(1.0)
C(1)–C(6)–C(7)–C(3)	−50.4(1.1)
C(6)–C(7)–C(8)–C(9)	7.2(1.6)
C(3)–C(7)–C(8)–C(9)	112.8(1.2)
C(14)–C(7)–C(8)–C(9)	−121.5(1.2)
C(6)–C(7)–C(8)–O(1)	−172.9(1.2)
C(3)–C(7)–C(8)–O(1)	−67.3(1.6)
C(14)–C(7)–C(8)–O(1)	58.4(1.6)
C(7)–C(8)–C(9)–C(10)	−80.0(1.6)
O(1)–C(8)–C(9)–C(10)	100.2(1.5)
O(1)–C(8)–C(9)–O(2)	−90.6(1.6)
C(7)–C(8)–C(9)–O(2)	89.3(1.6)
C(8)–C(9)–C(10)–C(11)	72.5(1.6)
O(2)–C(9)–C(10)–C(11)	−96.7(1.6)
C(9)–C(10)–C(11)–C(12)	−160.9(1.4)
C(9)–C(10)–C(11)–C(13)	80.3(1.5)
C(9)–C(10)–C(11)–C(1)	−42.6(1.6)
C(10)–C(11)–C(1)–C(2)	−56.7(1.4)
C(10)–C(11)–C(1)–C(6)	66.2(1.4)
C(12)–C(11)–C(1)–C(2)	61.8(1.5)
C(12)–C(11)–C(1)–C(6)	−175.3(1.3)

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[16] R. E. Marsh and J. Donohue, *Adv. Protein Chem.*, 1967, **22**, 235.

TABLE 3 (*Continued*)

C(13)–C(11)–C(1)–C(2)	–178.3(1.1)
C(13)–C(11)–C(1)–C(6)	–55.4(1.5)
C(11)–C(1)–C(6)–C(5)	155.5(1.0)
C(11)–C(1)–C(6)–C(7)	–100.2(1.1)
C(2)–C(1)–C(6)–C(5)	–75.2(1.2)
C(2)–C(1)–C(6)–C(7)	29.1(1.1)
C(2)–C(3)–C(7)–C(6)	53.2(1.1)
C(4)–C(3)–C(7)–C(6)	–56.4(1.0)
C(15)–C(3)–C(7)–C(6)	–179.2(1.0)
C(4)–C(3)–C(7)–C(8)	–172.9(1.0)
C(4)–C(3)–C(7)–C(14)	67.4(1.2)
C(15)–C(3)–C(7)–C(8)	64.3(1.3)
C(15)–C(3)–C(7)–C(14)	–55.4(1.4)
C(2)–C(3)–C(7)–C(8)	–63.3(1.2)
C(2)–C(3)–C(7)–C(14)	177.0(1.0)
Br–C(15)–C(3)–C(2)	–65.5(1.2)
Br–C(15)–C(3)–C(4)	58.4(1.2)
Br–C(15)–C(3)–C(7)	174.7(0.8)

C(7)–C(3)–C(4)–C(5) and C(7)–C(6)–C(5)–C(4) is zero in a structure possessing C_{2v} symmetry. In order to study the nature of the pseudorotation of the norbornane system a Newman projection down the non-bonded vector C(3) · · · C(6) is shown in Figure 2. According to the numbering system of ref. 14 the twist is *synchro-S*(+,+).

The energy minimization calculations of Bixon and Lifson [17] show that the energetically favourable conformation of a cyclo-heptane ring are skew chair, chair, boat, and skew boat with energies 5.55, 6.22, 7.95, and 8.19 kcal mol^{-1}. The present seven-membered ring corresponds very nearly to a chair conformation. It is interesting that the conformation of the seven-membered ring in longifolene hydrochloride [12] is the same as in the present structure, which has two carbonyl groups, whereas these are not present in the former.

The packing of the molecules in the unit cell is illustrated in Figure 3. The structure is stabilised mainly by van der Waals interactions.

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[17] M. Bixon and S. Lifson, *Tetrahedron*, 1967, **23**, 769.