Crystal structure of 2,2-*exo*-3,5,5-*exo*-6-hexabromobicycloheptane, $C_7H_6Br_6$

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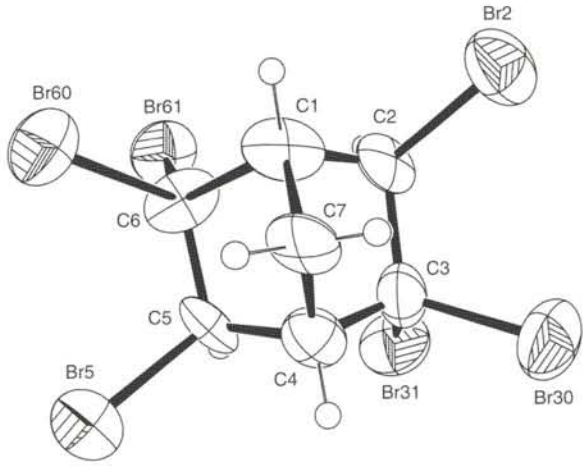

Abstract

$C_7H_6Br_6$, monoclinic, $P12_1/n1$ (No. 14), $a = 7.2717(7)$ Å, $b = 17.152(2)$ Å, $c = 10.0043(7)$ Å, $\beta = 97.722(7)°$, $V = 1236.5$ Å^3, $Z = 4$, $R_{gt}(F) = 0.086$, $wR_{obs}(F^2) = 0.227$, $T = 293$ K.

Source of material

2,5-dibromonorbornadiene was brominated at high temperature. After reaction we isolated the title compound by fractional crystallization. It was dissolved in boiling carbontetrachloride. The clear solution was cooled slowly to room temperature. In about 12 h, colorless rod-shaped crystals were obtained.

Discussion

Constitution and configuration of the products formed by electrophilic addition to norbornane and norbornadienes are interesting [1-4]. In connection with our continuing work in the temperature bromination reactions we have been interested in the bromination reaction of norbornadiene at room and at high temperature in order to see the effect of the temperature on skeletal rearrangement [5]. Recently we presented on alternative large-scale preparation of 2,5-dibromonorbornadiene by high temperature bromination of norbornadiene at 350 K in CCl_4 followed by dehydrobromination of nonrearranged addition products [6].

The topology of the norbornane moities in the title compound is consistent with that reported in other norbornanes. In particular, as observed in other norbornane derivatives (93.3(8)° [7], 94.3(4)° and 94.5(5)° [8], 94.4(4)° and 96.6(4)° [9], 96.2(3)°, 96.6(2)° and 96.7(2)° [10], 94.1(3)° and 94.0(2)° [11], 101.0(9)° [12]), the value of the C1–C7–C4 angle [94.3(7)°] is markedly different from the tetrahedral value. The C2—C3 and C5—C6 bond lengths are larger than the average value due to repulsive interaction between *cis*-bromine atoms connected to C2—C3 and C5—C6. The norbornane skeleton is composed of two fused five-membered rings in envelope conformation or of a six-membered ring held in a boat conformation by a bridging methylene group. Following the Cremer and Pople [13] notation the spherical polar set values (puckering parameters) for the six-membered rings are $Q = 0.909(3)$, $\theta = 88(2)°$, $\varphi = 177(2)°$. These values are very near to those corresponding to an ideal boat conformation ($\theta = 90°$, $\varphi = 180°$). The dihedral angles between the planar fragments C1-C2-C3-C4 (A), C4-C7-C1 (B) and C4-C5-C6-C1 (C) are 124(3)°, 121(3)° and 115(2)° for A-B, B-C and A-C respectively. They are comparable with those [113.9(6)°, 125.0(5)°, 121.1(5)°] determined for a similar derivative [14]. The deformations in the six-membered rings induced by the different substituents and by the methylene bridge with respect to the ideal values reported for a boat conformation [11] show some difference in the title compound. This difference reverberate on the internal torsion angles which, in going from C1 to C6 in numerical sequence are 1(3)°, 70(3)°, –73(3)°, 3(3)°, –69(3)° and –70(3)°. The steric repulsion between the bridging carbon (C7) and *exo*-bromine atoms (γ-Gauch effect) may cause extention of C1—C7 and C4—C7 bonds.

The average Br—C distance is 1.957(4) Å, Br–C–C angle is also 112.4(3)°. These values are 1.951(9)Å, 112.7(6)° in *exo,endo,exo,exo*-2,3,5,6-tetrabromonorbornane [15] and 1.960(14) Å, 111.2(4)° in *exo,endo,endo*-9,9,10,11,12-pentabromotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene [16], respectively. However, the structure has three intra-hydrogen bonds [C2–H2···Br61: 2.68(3) Å, 116(3)°, C5–H5···Br31: 2.50(3) Å, 120(3)°, C7–H7B···Br60: 2.90(3) Å, 107(3)°].

The extreme anisotropy of C1 and C6 may indicate a low quality of the investigated crystal.

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Table 1. Data collection and handling.

Crystal:	colorless, rod-shaped, size 0.20 × 0.30 × 0.35 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	231.09 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD-4, ω/2θ
$2\theta_{max}$:	153.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1673, 1491
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1318
$N(param)_{refined}$:	119
Programs:	SIR92 [17], SHELXS-93 [18], ORTEPII [19], PARST95 [20]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.751(4)	0.135(2)	0.209(3)	0.078
H(2)	4*e*	0.950(4)	0.050(2)	0.391(3)	0.067
H(4)	4*e*	1.289(4)	0.210(2)	0.271(3)	0.068
H(5)	4*e*	1.148(4)	0.208(2)	0.486(3)	0.060
H(7A)	4*e*	1.040(4)	0.158(2)	0.093(3)	0.077
H(7B)	4*e*	0.973(4)	0.240(2)	0.145(3)	0.077

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(2)	4*e*	0.9174(6)	–0.0118(3)	0.1744(4)	0.107(3)	0.080(4)	0.068(3)	–0.019(2)	0.025(2)	–0.018(2)
Br(30)	4*e*	1.3523(6)	0.0527(3)	0.2047(5)	0.091(2)	0.095(4)	0.116(4)	0.003(2)	0.056(2)	–0.017(3)
Br(31)	4*e*	1.3039(4)	0.0778(3)	0.5073(4)	0.067(2)	0.085(4)	0.079(3)	0.005(2)	–0.001(2)	0.015(2)
Br(5)	4*e*	1.1310(5)	0.3423(3)	0.3828(4)	0.085(2)	0.065(4)	0.073(3)	–0.009(2)	0.010(2)	–0.002(2)
Br(60)	4*e*	0.6948(5)	0.2846(3)	0.3125(4)	0.069(2)	0.087(4)	0.081(3)	0.018(2)	0.006(2)	0.006(2)
Br(61)	4*e*	0.8022(4)	0.1594(2)	0.5351(4)	0.070(2)	0.088(4)	0.052(3)	–0.004(2)	0.023(1)	–0.002(2)
C(1)	4*e*	0.875(4)	0.143(2)	0.258(3)	0.08(2)	0.11(3)	0.01(2)	–0.03(2)	0.00(1)	–0.01(1)
C(2)	4*e*	0.983(4)	0.067(2)	0.303(3)	0.08(2)	0.07(3)	0.03(2)	–0.02(1)	0.01(1)	–0.03(1)
C(3)	4*e*	1.194(4)	0.103(2)	0.323(4)	0.08(2)	0.05(3)	0.12(3)	–0.01(2)	0.06(2)	–0.02(2)
C(4)	4*e*	1.174(4)	0.185(2)	0.292(3)	0.07(2)	0.05(3)	0.05(2)	–0.01(1)	0.02(1)	0.00(1)
C(5)	4*e*	1.090(4)	0.226(2)	0.397(3)	0.08(2)	0.03(2)	0.04(2)	–0.02(1)	0.00(1)	–0.01(1)
C(6)	4*e*	0.881(3)	0.202(2)	0.376(2)	0.05(1)	0.10(3)	0.01(2)	0.00(1)	0.001(8)	0.02(1)
C(7)	4*e*	1.013(4)	0.188(2)	0.171(3)	0.07(2)	0.04(2)	0.08(2)	–0.03(2)	0.03(1)	0.02(2)

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