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X-ray Structure Analysis Online

Crystal Structure of (1*RS*,2*SR*,3*SR*,4*SR*,9*RS*)-1,2,3,9-Tetrabromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene

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In the title compound, $C_{11}H_8Br_4$, there is a norbornane skeleton with four Br atoms, having a benzene ring fused on one side. It crsytalizes in the orthorhombic *Pbca* space group. The unit-cell parameters at 294(2)K are a=11.9910(10), b=11.335(2), c=18.191(4)Å, V=2472.5(7)Å^3, D_x=2.470 g cm^{-3}, Z = 8.

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Great interest has been focused on the halogenation of norbornadiene[1] and benzonorbornadiene derivatives,[2–4] because these systems afford the possibilities of several mechanistically interesting investigations. These compounds are intriguing compounds in view of the di-π-methane rearrangement,[5] solvolytic reactivity and versatile purposes.[6] In view of this aspect, substituted benzonorbornadiene derivatives are important compounds that can provide information about how the substituents will influence the reaction modes. In addition to this, along with numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals, a bromine derivatives of a compound is worthy because it is a key for synthesizing other derivatives.

In this paper, we are interested in X-ray analyses of the tetrabromide (**4**). An izomer of (**4**), (1*RS*,2*RS*,3*SR*,4*SR*,9*RS*)-1,2,3,9-tetrabromo-1,2,3,4-tetrahydro-1,4-methanonaphthalene was recently published by Çelik *et al.*[7] The target molecule (**4**) was prepared by published methods[8] starting from 2,9-dibromobenzonorbornadiene (**1**) by high-temperature bromination.

To a magnetically stirred solution of (**1**) (1.28 g, 8.00 mmol) in refluxed CCl_4 (20 ml) was added dropwise a hot solution of bromine (1.52 g, 9.50 mmol) in hot CCl_4 (3 ml) during 5 min. The resulting reaction mixture was heated for 1 min at the reflux temperature. The solvent was evaporated and the residue was crystallized from CH_2Cl_2/pentane (1:2) and tetrabromide (**3**) was obtained (700 mg). After filtration of (**3**), the residue was chromatographed on silica gel (100 g) using hexane as an eluent. The first fraction was a mixture of tetrabromides (**2**) and (**3**). The solution was allowed to stand for a while in a refrigerator. The formed crystals were identified as tetrabromide (**2**). After filtration of the crystals, the residue was analyzed by NMR. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.51 – 7.24 (m, 4H, H_{aryl}), 4.41 (m, 1H), 4.38 (m, 1H), 4.35 (m, 1H), 3.99

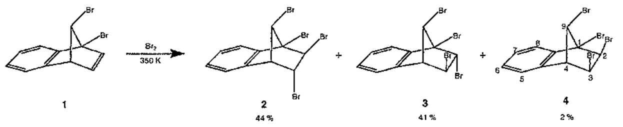

Fig. 1 Chemical diagram.

Table 1 Crystal and experimental data

Formula: $C_{11}H_8Br_4$
Formula weight = 459.77
Crystal system: orthorhombic
Space group: *Pbca* $Z = 8$
a = 11.9910(10)Å
b = 11.335(2)Å
c = 18.191(4)Å
V = 2472.5(7)Å^3
D_x = 2.470 g/cm^3
No. of reflections used = 2277
$2\theta_{max}$ = 51.4° with Mo K_α
R = 0.032
$(\Delta/\sigma)_{max} < 0.0001$
$(\Delta\rho)_{max}$ = 0.75 eÅ^{-3}
$(\Delta\rho)_{min}$ = –0.57 eÅ^{-3}
Data collection: COLLECT (Bruker AXS BV, 1997-2004).
Cell refinement: COLLECT
Data reduction: COLLECT
Absorption correction: multi-scan (based on symmetry-related measurements) (Blessing, 1995)
Structure determination: direct methods (SIR-97)
Refinement: full matrix least squares (SHELXL-97)
Molecular graphics: ORTEP-3 (Farrugia, 1997)
Software used to prepare material for publication: PLATON (Spek, 2003)

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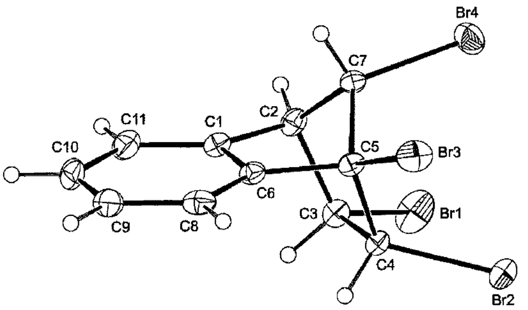

Fig. 2 ORTEP drawing of (**4**), along with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

Table 2 Atomic coordinates and temperature factors

Atom	x	y	z	U(eq)[Å^2]
Br1	0.29653(4)	−0.13967(5)	0.29876(2)	0.0535 (2)
Br2	0.13820(3)	−0.01431(4)	0.17062(2)	0.0376(2)
Br3	0.29261(3)	0.06522(4)	0.01971(2)	0.0400(2)
Br4	0.40763(4)	0.11825(4)	0.20493(2)	0.0425(2)
C1	0.4767(3)	−0.2035(3)	0.10496(19)	0.0266(9)
C2	0.4543(3)	−0.1361(3)	0.17491(19)	0.0271(10)
C3	0.3342(3)	−0.1730(3)	0.19622(18)	0.0278(10)
C4	0.2593(3)	−0.1146(3)	0.13608(18)	0.0230(9)
C5	0.3478(3)	−0.0525(3)	0.08652(17)	0.0227(9)
C6	0.4089(3)	−0.1537(3)	0.04981(18)	0.0244(9)
C7	0.4410(3)	−0.0140(3)	0.13992(19)	0.0249(9)
C8	0.4061(3)	−0.1994(4)	−0.02031(19)	0.0321(11)
C9	0.4729(3)	−0.2962(4)	−0.0353(2)	0.0380(11)
C10	0.5414(3)	−0.3451(4)	0.0181(2)	0.0380(11)
C11	0.5440(3)	−0.2999(3)	0.0892(2)	0.0345(11)

U(eq) = 1/3 of the trace of the orthogonalized U tensor.

Table 3 Selected bond distances (Å) and angles (°)

Br1–C3	1.956 (3)	Br3–C5	1.922 (3)
Br2–C4	1.948 (4)	Br4–C7	1.951 (3)
Br1–C3–C2	113.7 (2)	Br3–C5–C6	114.4 (2)
Br1–C3–C4	116.9 (2)	Br3–C5–C7	116.8 (2)
Br2–C4–C3	116.7 (2)	Br4–C7–C2	117.6 (2)
Br2–C4–C5	115.5 (2)	Br4–C7–C5	116.8 (2)
Br3–C5–C4	116.4 (2)		

(m, 1H, H4). ^{13}C-NMR (50 MHz, CDCl$_3$): δ 145.0, 143.4, 131.6, 131.0, 124.94, 123.4, 69.8, 62.5, 59.2, 57.2, 52.0. IR (KBr, cm^{-1}): ν 3030, 3004, 2979, 1472, 1447, 1294, 1268, 1243, 1166, 987, 910, 757. Analysis calculated for $C_{11}H_8Br_4$: C 28.73, H 1.75%. Found: C 28.53, H 1.69%. M. p. 459 – 460 K. Crystals of (**4**) suitable for X-ray analysis were obtained by slow evaporation of a CH_2Cl_2/pentane (1:2) solution at room temperature. The crystal and molecular structures of the title compound were elucidated by single-crystal X-ray diffraction.

A summary of the crystallographic information is given in Table 1. The data were collected on a Nonius Kappa CCD diffractomer with an imaging-plate detector diffractometer using graphite-monochromated Mo K_α radiation with the ϕ and ω scan mode. The collected data were reduced by using the COLLECT program, and an absorption correction using a multi-scan technique was applied. The title compound was solved by direct methods and refined by a full-matrix least-squares method on F^2. All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93 or 0.98 Å for aromatic and methine H atoms, respectively, and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. The final conventional $R(F)$ converged to 0.032. The atomic coordinates and equivalent isotropic displacement parameters along with the estimated standard deviations for the other atoms, except for H, are listed in Table 2. Selected geometric parameters are given in Table 3. An ORTEP-3 drawing of the title compound with the atom numbering is shown in Fig. 2.

In the norbornane fragment of (**4**) in Fig. 1, the six-membered ring (C1 – C6) exhibits a boat conformation [the puckering parameters: Q_T=0.994(4)Å, ϕ_2=241.0(2)° and θ_2=89.4(2)°]. The two five-membered rings A (C1/C2/C7/C5/C6) and B (C2/C3/C4/C5/C7) have envelope conformations, with atom C7 as the flap. The related puckering parameters are Q_2= 0.602(4)Å and ϕ_2 = 70.7(4)° for ring A, and Q_2 = 0.537(4)Å and ϕ_2 = 142.7(4)° for ring B. The dihedral angles between the planes C (C1/C2/C5/C6/C8 - C11) [max. deviations from the planarity of –0.033(4) and –0.020(4)Å for C2 and C9, respectively], D (C2/C5/C7) and E (C2 - C5) [max. deviations form the planarity of –0.006(3)Å for C3 and 0.006(3)Å for C5] are C/D = 57.34(20)°, C/E = 72.03(12)° and D/E = 50.64(22)°. The average Br–C bond value of 1.944(4)Å and the average Br–C–C angle value of 116.1(2)° are comparable with those of the similar compounds.[9]

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