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Structure of *exo,endo,endo*-9,9,10,11,12-Pentabromotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5-triene

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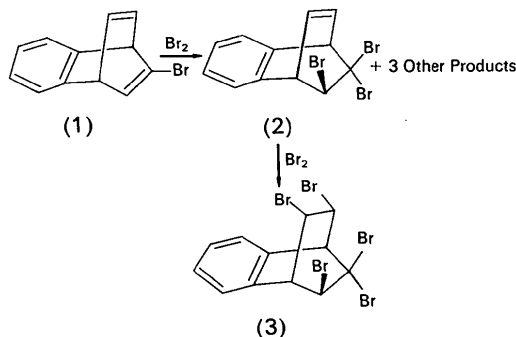
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Abstract. C₁₂H₉Br₅, *M*_r = 552.723, triclinic, *P* $\bar{1}$, *a* = 10.441 (1), *b* = 12.406 (1), *c* = 6.887 (1) Å, α = 90.82 (1), β = 124.01 (1), γ = 102.73 (1)°, *V* = 710.8 Å³, *Z* = 2, *D*_m = 2.56, *D*_x = 2.582 g cm⁻³, $\lambda(\text{Cu K}\alpha)$ = 1.54180 Å, μ = 171.38 cm⁻¹, *F*(000) = 512, *T* = 293 K, *R* = 0.034 for 2045 observed reflections. X-ray analysis of the title compound shows that the skeleton of the molecule is not changed after two successive bromination reactions. The addition of the second Br₂ molecule occurs contrary to our expectation in a *syn* fashion. This is probably due to interactions with neighbouring Br atoms.

Introduction. Benzobarrelene (1,4-dihydro-1,4-ethenonaphthalene) is an ideal compound for di- π -methane rearrangement (Hixon, Mariano & Zimmerman, 1973). In particular, the introduction of a substituent in a vinyl location increases the number of possible initial bonding modes. Therefore, one may obtain more insight into the mechanism of the di- π -methane rearrangement and the effect of substituents. Recently, an efficient synthetic route leading to monosubstituted benzobarrelene derivatives has been developed (Balci, Çakmak & Harmandar, 1985). As an extension of this work, an alternative large-scale preparation of disubstituted benzobarrelene derivatives has been undertaken (Çakmak & Balci, 1989). We were also interested in the synthesis of trisubstituted benzobarrelenes (Çakmak, Hökelek & Balci, 1990).

For this purpose we carried out the bromination of (1) refluxing in CCl₄ and isolated four bromination products. One of these, isomer (2), was subjected to further bromination and only one isomer was obtained. In order to gain more knowledge of the reaction mechanism and the structure of the product, we carried out an X-ray structure analysis of isomer (3).



Experimental. The compound was dissolved in boiling chloroform and *n*-hexane added. The clear solution was cooled slowly at room temperature. In about 6 h, the colourless rod-shaped crystals (m.p. 453 K) were obtained.

Initially, the cell had the parameters *a* = 6.887, *b* = 8.718, *c* = 12.406 Å and α = 74.03, β = 89.18, γ = 83.10° with the matrix elements 00 $\bar{1}$, $\bar{1}0\bar{1}$, 010. But we re-refined the standard cell with the matrix

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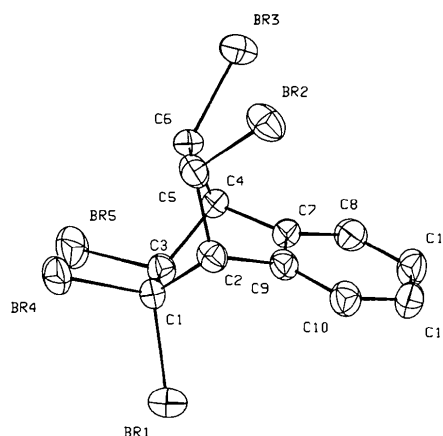
Table 1. *Experimental data and structure-refinement parameters*

Method of measuring D_m	Pycnometer (H ₂ O)
Crystal shape and size (mm)	Rod-shaped, 0.05 × 0.09 × 0.2
Diffractometer used and data-collection technique	Four-circle diffractometer (Enraf-Nonius CAD-4), ω - 2θ scan
Number and θ range of reflections used for measuring lattice parameters	25 reflections with $12 \leq 2\theta \leq 32^\circ$
Absorption correction applied (with max. and min. values)	Semi-empirical (North, Phillips & Mathews, 1968); 2.78 and 2.36
Maximum value of 2θ ($^\circ$) and $(\sin\theta/\lambda)$ (\AA^{-1}) reached in intensity measurements	72 and 0.617
Range of h , k and l	$-1 \leq h \leq 12$, $-15 \leq k \leq 15$, $-8 \leq l \leq 8$
Standard reflections and their intensity variations throughout experiment	$\bar{2}12$, $1\bar{1}1$, 040 ; variation 2, 2, 0%, respectively
Number of reflections measured	3378
Number of unique reflections	2797
Number of unobserved reflections	752
Criterion for recognizing unobserved reflections	$I \leq 3\sigma(I)$
Method used to solve structure	Direct methods
Use of F or F^2 magnitudes in least-squares refinement	F
Parameters refined	(Coordinates and anisotropic temperature factors of non-H atoms) 154
Values of R , wR and R_{int}	0.034, 0.042 and 0.000
S (goodness of fit)	4.28
Method used to calculate w	Chebyshev
Final residual electron density (e \AA^{-3}) for max. and min. peaks	+4.25 and -4.25
Max. (Δ/σ)	0.00
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974)
Computer programs used	<i>SHELXS86</i> (Sheldrick, 1986), <i>CRYSTALS</i> (Watkin, Carruthers & Betteridge, 1985), <i>SNOOPI</i> (Davies, 1982)

Table 2. *Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C1	3406 (6)	7345 (4)	1660 (9)	327
C2	1778 (6)	7631 (4)	491 (9)	327
C3	3967 (6)	7497 (4)	-6 (9)	334
C4	2559 (6)	7615 (4)	-2494 (9)	308
C5	496 (6)	6690 (5)	-1712 (10)	344
C6	1074 (6)	6619 (4)	-3335 (9)	325
C7	2226 (6)	8686 (4)	-2122 (9)	306
C8	2321 (6)	9625 (5)	-3181 (10)	378
C9	1888 (6)	8714 (4)	-435 (9)	308
C10	1648 (7)	9678 (5)	205 (11)	384
C11	2064 (7)	10570 (5)	-2542 (12)	411
C12	1745 (7)	10605 (5)	-863 (12)	438
Br1	4996.2 (7)	8417.7 (5)	4638 (1)	426
Br2	-1598.2 (7)	6992.2 (6)	-3154 (1)	453
Br3	-534.9 (7)	6525.8 (6)	-6753 (1)	446
Br4	3221.1 (8)	5872.2 (5)	2616 (1)	445
Br5	4896.1 (9)	6358.1 (6)	-294 (1)	505

Fig. 1. A *SNOOPI* (Davies, 1982) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

elements $1\bar{1}0$, 001 , $\bar{1}00$ and obtained the cell parameters reported here.

The method employed to solve the structure and other related parameters and procedures are given in Table 1. Non-H atoms were included with anisotropic thermal parameters. Difference syntheses did not show clearly the electron density for H atoms. Therefore, H atoms were geometrically positioned 1.0 Å from C atoms with coordinates and isotropic temperature-factor coefficients ($U = 0.05 \text{\AA}^2$) kept fixed in the refinement process.

Discussion. The final coordinates and isotropic or equivalent isotropic thermal parameters are given in Table 2.* The structure of the title compound is shown in Fig. 1. It contains the expected benzo-bicyclo[2.2.2]octane skeleton. The bond lengths and

angles, given in Table 3, agree with those observed in C₁₂H₉Br₃ (Hökelek, Çakmak & Balci, 1990). There is an approximately tetrahedral environment about the C1 atom, but the Br1—C1—Br4 angle [$105.4(2)^\circ$] is smaller and the Br4—C1—C3 angle [$116.2(4)^\circ$] is larger than the conventional value of the tetrahedral angle. The C1—C3—Br5 angle [$116.3(3)^\circ$] is also larger than the other angles about C3. This behaviour appears to be a result of a repulsive interaction between Br4 and Br5. Similarly, the Br2—C5—C6 [$116.6(3)^\circ$] and Br3—C6—C5 [$116.3(3)^\circ$] angles are larger than the other angles about C5 and C6 respectively, probably because of the repulsion between Br2 and Br3 atoms. The sums of the angles about C7 and C9 are $359.8(5)^\circ$ and $360.0(5)^\circ$ respectively, so the atoms attached to them lie in a plane with the corresponding values of the bond angles given in Table 3. The residual electron

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52921 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and bond angles (°) with *e.s.d.*'s in parentheses

C1—C2	1.552 (7)	C5—C6	1.548 (8)
C1—C3	1.551 (8)	C5—Br2	1.963 (5)
C1—Br1	1.968 (5)	C6—Br3	1.965 (5)
C1—Br4	1.958 (5)	C7—C8	1.398 (7)
C2—C5	1.564 (8)	C7—C9	1.393 (8)
C2—C9	1.505 (7)	C8—C11	1.376 (9)
C3—C4	1.550 (7)	C9—C10	1.388 (8)
C3—Br5	1.947 (5)	C10—C12	1.390 (8)
C4—C6	1.549 (7)	C11—C12	1.37 (1)
C4—C7	1.498 (7)		
C3—C1—C2	109.4 (4)	Br1—C1—C2	107.7 (4)
Br1—C1—C3	108.3 (4)	Br4—C1—C2	109.3 (4)
Br4—C1—C3	116.2 (4)	Br4—C1—Br1	105.4 (2)
C5—C2—C1	106.7 (4)	C9—C2—C1	108.8 (4)
C9—C2—C5	107.1 (4)	C4—C3—C1	109.4 (4)
Br5—C3—C1	116.3 (3)	Br5—C3—C4	110.4 (4)
C6—C4—C3	108.2 (4)	C7—C4—C3	105.4 (4)
C7—C4—C6	109.4 (4)	C6—C5—C2	108.7 (4)
Br2—C5—C2	107.7 (4)	Br2—C5—C6	116.6 (3)
C5—C6—C4	110.5 (4)	Br3—C6—C4	108.9 (3)
Br3—C6—C5	116.3 (3)	C8—C7—C4	126.3 (5)
C9—C7—C4	113.3 (4)	C9—C7—C8	120.2 (5)
C11—C8—C7	119.0 (6)	C7—C9—C2	114.1 (5)
C10—C9—C2	125.9 (5)	C10—C9—C7	120.0 (5)
C12—C10—C9	119.2 (6)	C12—C11—C8	121.0 (5)
C11—C12—C10	120.6 (6)		

density is high, probably due to the repulsions between Br atoms in the structure.

The X-ray structure analysis of the title compound has revealed that bromine addition has occurred in (3) contrary to our expectation in a *syn* fashion. Studies concerning the mechanism of *syn* addition show that the *syn* adduct can arise either from direct *syn* collapse of the ion pair or from rotation followed by anti-collapse (Heasley, Bower, Dougharty & Easdon, 1980). Because of the rigid skeleton in (2) a bond rotation is out of the question. Another

possible mechanism for *syn* addition is the effect of the neighbouring Br atom at C3 which can attack the preliminary formed cyclic bromonium ion from the underside. The Br ion attacks the cyclic bromonium ion from the *syn* face of the molecule to give the *syn* adduct (3).

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Structure of 5,19-Diamino-9,12,15-trioxatricyclo[14.4.0.0^{3,8}]jicosa-1(16),3,5,7,17,19-hexaene

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Abstract. C₁₇H₂₀N₂O₃, *M_r* = 300.356, monoclinic, *P*2₁/*c*, *a* = 14.443 (2), *b* = 13.883 (2), *c* = 7.455 (3) Å,

$\beta = 94.08 (2)^\circ$, *V* = 1491.0 (2) Å³, *Z* = 4, *D_m* = 1.3, *D_x* = 1.338 g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54180 \text{ \AA}$, $\mu = 7.119 \text{ cm}^{-1}$, *F*(000) = 640, *T* = 293 K, *R* = 0.038 for 2384 observed reflections. The title compound adopts

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