

There is no evidence of enolization in the molecule; C(1)—O(1) [1.216 (4) Å] and C(5)—O(5) [1.237 (4) Å] are typical of carbonyl bond lengths as described by Amorese, Gavuzzo, Mazza, Casini & Ferappi (1982) and by Onan, Rao & Parry (1985). This is noteworthy because proton NMR spectroscopy suggests that in DMSO solution there exists a pair of keto-enol tautomers, the more dominant being the enol form (approx. 60%). Also typical are the bond lengths N(2)—C(1) and N(2)—C(5) of 1.375 (4) and 1.370 (4) Å, respectively, implying some delocalization across the imide system. Such delocalization explains why N(2) is trigonal, with the O(1)—C(1)—N(2)—N(1)—C(5)—O(5) system being planar (r.m.s. deviation 0.008 Å).

The C(11)—C(6)—C(7) angle in the benzene ring is unusually small [115.6 (3)°], probably due to a number of factors: the repulsions between the H atom on C(11) and those on C(2), the repulsion between ring and alkene π clouds and the inductive effect caused by the release of electrons along the C(3)—C(6) bond towards C(6) may all contribute.

With such repulsive interactions and without any ring-ring stabilization, it is perhaps surprising that the molecule adopts such a planar conformation. It is, however, possible to rationalize this on three counts. Firstly there exists the possibility of a hydrogen bond between H(4) and O(7) [2.11 (3) Å], secondly when the symmetry related molecule at $-x, 2-y, 1-z$ is considered it is apparent that the two molecules are oriented such that all four rings are coplanar. The proton on O(7) forms a strong hydrogen bond [1.85 (4) Å] to the carbonyl O(5)' of the

second molecule [angle H(7)—O(7)—O(5)' 15 (3)°]. Similarly, the O(7)' H atom on the second molecule bonds to O(5) of the first. Consistent with this hydrogen-bonding model, the C(5)—O(5) bond is some 0.021 (4) Å longer than the C(1)—O(1) bond. The third contribution may arise from packing forces which encourage planar packing within the crystal. It appears that the sum of these effects is strong enough to overcome the steric and electronic repulsions which tend to induce torsional asymmetry.

For comparison, biphenyl is also apparently planar in the solid (Charbonneau & Delugeard, 1977) and the endocyclic angle at the ring to ring bond is 117.3 (2)°.

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Structure of *exo,exo*-9,10,12-Tribromotricyclo[6.3.1.0^{2,7}]dodeca-2(7),3,5,10-tetraene

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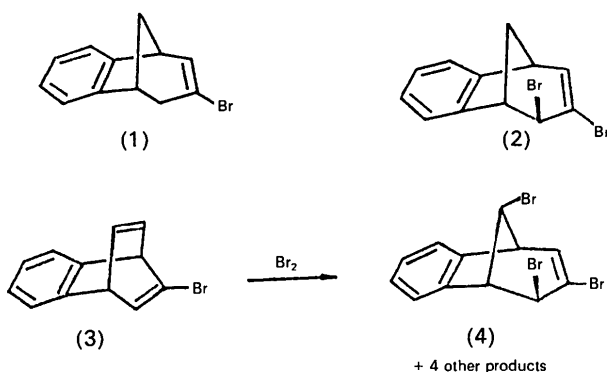
Abstract. C₁₂H₉Br₃, $M_r = 392.915$, orthorhombic, $P2_12_12_1$, $a = 6.979$ (4), $b = 9.596$ (1), $c = 18.056$ (4) Å, $V = 1209.22$ Å³, $Z = 4$, $D_m = 2.1$, $D_x = 2.158$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54180$ Å, $\mu(\text{Cu } K\alpha) =$

122.24 cm⁻¹, $F(000) = 744$, $T = 293$ K, $R = 0.044$ for 1254 observed reflections. In the title compound, the Br(1)—C(12) [1.966 (9) Å] and Br(3)—C(9) [1.971 (7) Å] distances are almost equal but Br(2)—C(10) [1.892 (7) Å] is shorter. The structural analysis has revealed that the starting compound,

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9-bromotricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentane, a [2.2.2] system, has rearranged to the title compound, a [3.2.1] system, *via* an aryl shift.

Introduction. It has been shown that the electrophilic attack of Br on unsaturated bicyclic systems can lead to a multiplicity of products. Attack at the double bond may be *endo* or *exo*. The intermediate bromonium ion can react with nucleophiles to give non-rearranged products or react to give Wagner–Meerwein rearrangement (Balci & Harmandar, 1988). Recently, the bromination reactions of (1) and (2) have been studied and the structures of the products formed have been determined (Balci & Harmandar, 1988; Çakmak & Balci, 1989).



It has been shown that the reaction temperature has a strong influence on product distribution. This effect has been interpreted on the basis of the lifetime of the initially formed bromonium ion. As an extension of this work, the bromination of (3) has been investigated in order to compare the behaviour of a [2.2.2] bicyclic system (3) with the [3.2.1] systems of (1) and (2).

Experimental. The title compound was prepared by bromination of (3), according to the following procedure. Compound (3) (1.1 g, 4.72 mmol) in 50 ml of pentane was reacted with Br (0.76 g, 4.74 mmol) in 15 ml of pentane at 273 K. Analysis of the reaction mixture revealed the formation of five isomeric products. One of these isomers crystallized during the reaction. After separation of this isomer, the residue was subjected to column chromatography using silica gel (100 g) by eluting with petroleum ether/chloroform (7:1). The last fraction obtained was compound (4) in a yield of 3%. It was dissolved in boiling chloroform with added *n*-hexane. The clear solution was cooled slowly to room temperature. In about 6 h, colourless rod-shaped crystals (m.p. 398–399 K) were obtained.

Experimental data, methods used to solve the structure and other related data and procedures are

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

Method of measuring D_m	Pycnometer (H ₂ O)
Crystal shape and size (mm)	Rod-shaped, 0.12 × 0.24 × 0.94
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 $36 \leq 2\theta \leq 64$
Absorption correction applied (max. and min. values)	Semi-empirical (North, Phillips & Mathews, 1968) (2.75 and 2.36) 0.617
Maximum value of $(\sin\theta/\lambda)$ (\AA^{-1}) reached in intensity measurements	$-1 \leq h \leq 8$, $-1 \leq k \leq 11$, $-1 \leq l \leq 22$
Range of h , k and l	301, 402, 260 variation 0, 1, 0, respectively
Standard reflections and their intensity variation (%) throughout experiment	1992
Number of reflections measured	1398
Number of unique reflections	144
Number of unobserved reflections	144
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, 135
Values of R , wR , R_{int}	0.044, 0.052, 0.00
S (goodness of fit)	S not calculated
Method used to calculate w	Chebyshev
Final residual electron density ($e \text{\AA}^{-3}$) for max. and min. peaks	+ 3.77 and - 3.77
Max. (Δ/σ)	0.00
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
Computer programs used	SHELXS86 (Sheldrick, 1986). CRYSTALS (Watkin, Carruthers & Betteridge, 1985), SNOOPI (Davies, 1983)

given in Table 1. Non-H atoms were refined anisotropically. The H-atom positions could not be determined from difference Fourier analysis. Therefore, H atoms were geometrically positioned 1.080 Å from C atoms. H-atom coordinates with isotropic temperature-factor coefficients ($U = 0.0482 \text{\AA}^2$) were fixed in the refinement process.

The high residual electron density seems to be due to the repulsions between Br atoms in the structure and also to extinction effects. Initially a unit weighting scheme was used, but in the final stages of refinement the weights were assigned using the method described by Carruthers & Watkin (1979) as incorporated into the CRYSTALS package of programs (Watkin, Carruthers & Betteridge, 1985).

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. Bond lengths, bond angles and selected torsion angles are listed in Table 3.*

In the five-membered C(1)—C(2)—C(7)—C(8)—C(12) ring, the sum of the bond angles is $513.6(7)^\circ$. Three of the angles [C(7)—C(8)—C(12)] $98.3(6)$,

* 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 53807 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

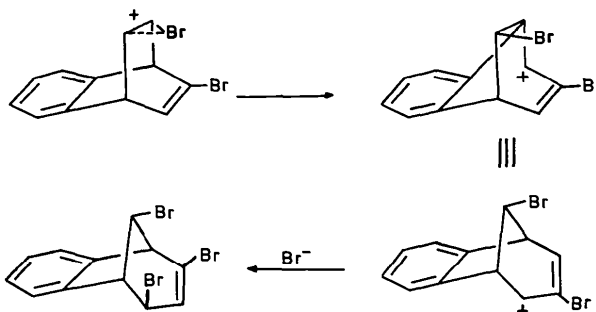
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (\AA^2)
Br(1)	2217 (1)	1712 (1)	3587.3 (3)	575
Br(2)	-3774 (2)	4258.3 (9)	3243.0 (6)	600
Br(3)	-1263 (2)	1911 (1)	2104.9 (5)	578
C(1)	-1457 (13)	137 (8)	3399 (4)	398
C(2)	-2834 (13)	-511 (7)	3959 (4)	372
C(3)	-4215 (16)	-1541 (9)	3866 (5)	491
C(4)	-5319 (17)	-1896 (10)	4456 (6)	574
C(5)	-5118 (16)	-1249 (10)	5140 (5)	515
C(6)	-3738 (14)	-209 (9)	5236 (5)	453
C(7)	-2622 (13)	144 (8)	4642 (4)	378
C(8)	-1052 (13)	1233 (8)	4570 (4)	396
C(9)	-2418 (13)	1407 (8)	3063 (4)	373
C(10)	-2538 (12)	2625 (7)	3584 (4)	369
C(11)	-1914 (11)	2560 (7)	4279 (4)	342
C(12)	136 (14)	522 (9)	3959 (5)	455

Table 3. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses and selected torsion angles ($^\circ$)

Br(1)—C(12)	1.966 (9)	C(4)—C(5)	1.39 (1)
Br(2)—C(10)	1.892 (7)	C(5)—C(6)	1.40 (1)
Br(3)—C(9)	1.971 (7)	C(6)—C(7)	1.37 (1)
C(1)—C(2)	1.53 (1)	C(7)—C(8)	1.52 (1)
C(1)—C(9)	1.52 (1)	C(8)—C(11)	1.50 (1)
C(1)—C(12)	1.55 (1)	C(8)—C(12)	1.54 (1)
C(2)—C(3)	1.39 (1)	C(9)—C(10)	1.50 (1)
C(2)—C(7)	1.39 (1)	C(10)—C(11)	1.33 (1)
C(3)—C(4)	1.36 (2)		
C(2)—C(1)—C(9)	108.3 (7)	C(7)—C(8)—C(11)	108.9 (7)
C(2)—C(1)—C(12)	96.7 (6)	C(7)—C(8)—C(12)	98.3 (6)
C(9)—C(1)—C(12)	112.8 (6)	C(11)—C(8)—C(12)	109.9 (6)
C(1)—C(2)—C(3)	130.2 (8)	C(1)—C(9)—C(10)	113.5 (6)
C(1)—C(2)—C(7)	109.6 (7)	C(1)—C(9)—Br(3)	111.6 (6)
C(3)—C(2)—C(7)	120.2 (2)	C(10)—C(9)—Br(3)	112.5 (6)
C(2)—C(3)—C(4)	118.4 (9)	C(9)—C(10)—C(11)	122.4 (7)
C(3)—C(4)—C(5)	121.9 (9)	C(9)—C(10)—Br(2)	117.8 (6)
C(4)—C(5)—C(6)	119.9 (9)	C(11)—C(10)—Br(2)	119.7 (6)
C(5)—C(6)—C(7)	118.2 (8)	C(8)—C(11)—C(10)	120.0 (6)
C(6)—C(7)—C(2)	121.5 (8)	C(1)—C(12)—C(8)	100.8 (7)
C(6)—C(7)—C(8)	130.4 (8)	C(1)—C(12)—Br(1)	112.6 (6)
C(8)—C(7)—C(2)	108.2 (7)	C(8)—C(12)—Br(1)	116.5 (6)
Br(1)—C(12)—C(1)—C(2)	170.1	Br(2)—C(10)—C(9)—C(1)	178.1
Br(1)—C(12)—C(8)—C(11)	172.6	Br(3)—C(9)—C(10)—C(11)	130.0
Br(1)—C(12)—C(1)—C(9)	57.0	Br(3)—C(9)—C(1)—C(2)	158.9
Br(1)—C(12)—C(8)—C(11)	59.0	Br(3)—C(9)—C(1)—C(12)	95.3
Br(2)—C(10)—C(11)—C(8)	175.8		

C(8)—C(12)—C(1) 100.8 (7), C(12)—C(1)—C(2) 96.7 (6) $^\circ$] are narrow while the remaining angles [C(1)—C(2)—C(7) 109.6 (7), C(2)—C(7)—C(8) 108.2 (7) $^\circ$] have normal values. Similar angular values have also been reported for the five-membered ring in an analogous compound (Büyükgüngör, Harmandar & Balcı, 1989). The strain in the structures containing one atom on the bridge is more predominant than in structures containing two C atoms on the bridge (Hökelek, Çakmak & Balcı, 1990). C(10)—C(11) [1.33 (1) \AA] has double-bond character and the average value of the C—C bond lengths in the benzene ring is 1.38 (1) \AA . As can be seen from Table 3, the dihedral angles Br(1)—C(12)—C(8)—C(11) (59.0), and Br(1)—C(12)—C(1)—C(9) (57.0 $^\circ$) indicate the position of Br(1) above the non-aromatic six-membered ring. Br(3) is

on the same side of that ring as Br(1) [Br(3)—C(9)—C(1)—C(12) 95.3 $^\circ$] and in a *trans* position with respect to C(2) [Br(3)—C(9)—C(1)—C(2) 158.9 $^\circ$]. This orientation can only be explained by *exo* attack of the Br atom at the unsubstituted double bond as shown below.



endo attack should give alkyl-shift products instead of the aryl-shift products. Therefore, Br(1) has to have the *exo* orientation in this structure as expected. Br(2) is in the plane of the double bond, [Br(2)—C(10)—C(11)—C(8) 175.8, Br(2)—C(10)—C(9)—C(1) 178.1 $^\circ$], while Br(3) is in the *exo* configuration with respect to C(12). Br(1)—C(12) [1.966 (9) \AA] and Br(3)—C(9) [1.971 (7) \AA] are nearly equal. However, Br(2)—C(10) [1.892 (7) \AA] is significantly shorter than the other distances; this is probably due to electron transfer from Br(2) to the C(11)—C(10) (1.33 \AA) double bond. All of the other C—C single-bond lengths of the molecule range from 1.50 (1) to 1.55 (1) \AA with a mean value of 1.52 (1) \AA . The X-ray structure analysis reveals that the title compound (4) is a rearranged product. Compound (3), a [2.2.2] system, has rearranged to compound (4), a [3.2.1] system.

It is also clear that the attack of Br occurred at the unsubstituted double bond. In addition, this new product (4) has to be formed by an aryl shift following the preliminary formation of the bromonium ion.

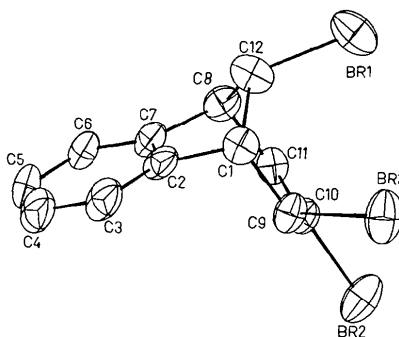


Fig. 1. A SNOOPI (Davies, 1983) drawing of the title molecule with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

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Synthesis of Hydrophenanthrene Natural Products. Structure of a 17-Nordehydropimarane Derived from Dehydroabietic Acid*

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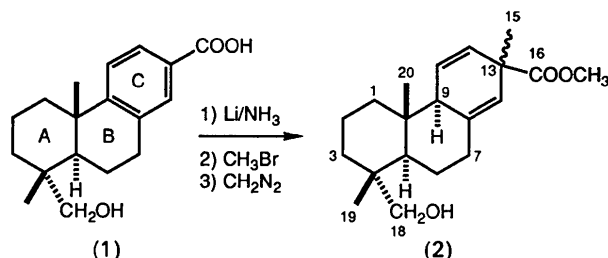
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Abstract. $C_{20}H_{30}O_3$, $M_r = 318.46$, triclinic, $P1$, $a = 7.108$ (1), $b = 7.362$ (5), $c = 9.112$ (2) Å, $\alpha = 96.21$ (4), $\beta = 89.85$ (1), $\gamma = 106.31$ (2)°, $V = 454.8$ Å³, $Z = 1$, $D_x = 1.16$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.82$ cm⁻¹, $F(000) = 174$, $T = 293$ K, final $R = 0.046$ for 852 observed [$F_o \geq 5\sigma(F_o)$] reflections. The structure reveals a *trans* relationship between the hydrogen at C(9) and the methyl group C(20) as well as an *R* absolute stereochemistry at C(13). Intermolecular hydrogen-bonded chains along the unit-cell edge *c* characterize the crystal lattice.

Introduction. Our interest in the chemistry and biology of hydrophenanthrene natural products has prompted us to investigate the conversion of dehydroabietic acid to diterpenes which may be represented by the pimarane skeleton. Dehydroabietic acid, an abundant abietane diterpene and the major

constituent of commercial rosin, has been used previously as a synthon (Ohsawa, Ohtsuka, Nakata, Akita & Shimagaki, 1976; Buchbauer & Kolbe, 1985) but to date has not been transformed to a pimarane natural product. A reductive alkylation of the aromatic *C* ring of 13-carboxydeisopropyldehydroabietanol, (1), was seen as the key step in this transformation. In one step from a 13-carboxy derivative (Ohta, 1956) we envisioned, after alkylation with methyl bromide (see below), the creation of two features prerequisite for transformation to the pimarane skeleton: a quaternary methyl at C(13) and the necessary *trans-anti ABC* ring juncture formed after introduction of the hydrogen at C(9)



* The *Chemical Abstracts* name is: [2*R*-(2 α ,4 α ,8 β ,8 α)]-2,4 α ,4 β ,5,6,7,8,8 α ,9,10-decahydro-8-(hydroxymethyl)-2,4 β ,8-trimethyl-2-phenanthrenecarboxylic acid methyl ester. For the remainder of this paper the more common steroid numbering scheme, as indicated in the reaction scheme, will be used.

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