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# Low-Temperature Structure of 1,2,3,4,5,6,7,8-Octahydroanthracene, $C_{14}H_{18}$

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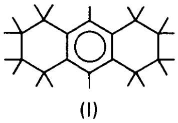
**Abstract.** $M_r = 186.30$, monoclinic, $P2_1/c$, $a = 9.354$ (3), $b = 6.550$ (2), $c = 9.622$ (3) Å, $\beta = 116.99$ (3)°, $V = 525.3$ Å$^3$, $Z = 2$, $D_x = 1.18$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.071$ mm$^{-1}$, $F(000) = 204$, $T \simeq 110$ K. Final $R = 0.038$ for 1593 observed data. There is a good correspondence between the experimentally determined values of the bond lengths, bond angles and torsion angles and the estimates of these values from molecular-mechanics calculations on the achiral conformation.

**Introduction.** Empirical force-field calculations on 1,2,3,4,5,6,7,8-octahydroanthracene (I) reveal the existence of two equally stable conformations. Depending on the mutual orientation of the half-chair forms of the outer cyclohexene rings the point group is $2/m$ (achiral) or 222 (chiral) (Baas, unpublished results). The present paper describes the low-temperature form (the α form) of the title compound (I). It is designated as the α form because at 318K a martensite-type transformation to a $\beta$ form is observed (Vatulev & Prikhot'ko, 1965).



(I)

**Experimental.** (I) obtained from Dr D. Tavernier (University of Gent, Belgium), recrystallized from acetone at 278 K. Crystal of approximate dimensions 0.3 × 0.4 × 0.4 mm enclosed in a thin-walled capillary and cooled down by a cold $N_2$ gas stream to 110 (2) K. Systematic absences, $h0l$ for $l$ odd and $0k0$ for $k$ odd, indicated space group $P2_1/c$. Cell parameters obtained from diffractometer angular settings of 25 centered reflections. Data collected for $hk \pm l$ ($h_{\max} = 13$, $k_{\max} = 9$, $l \pm 14$) with $\theta_{\max} = 32.00°$ on a Nonius CAD-4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation). These gave 1817 independent data of which 1593 reflections with $I > \sigma(I)$ used in subsequent calculations. Three reflections measured every 2 h of X-ray exposure time, intensity variation within 3%. Extinction and absorption neglected. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971); H atoms located in a difference map. Refinement ($x$, $y$, $z$ of all atoms, anisotropic temperature factors for heavy atoms, isotropic for H) by full-matrix least squares on $F$ (XRAY72, Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with equal weights given to all reflections converged at $R = 0.038$. In final cycle shifts in parameters all $< 0.1\,\sigma$. Final difference map showed peaks of about 0.40 e Å$^{-3}$ halfway between bonded C atoms. Molecular-mechanics calculations performed using *DELPHI* (van de Graaf, Baas & van Veen, 1980), empirical force field from Brückner, Allegra, Albinati & Ferina (1980).

**Discussion.** Positional and isotropic thermal parameters are given in Table 1.* The structure is shown in Fig. 1 with the atom numbering used here. Bond lengths, bond angles and torsion angles of the carbon skeleton are given in Fig. 2 together with the values obtained with the empirical force-field calculations. All observed

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38924 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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C—H bond lengths are equal to 1·00 Å within $2\sigma\,[\sigma(\text{C—H}) \simeq 0{\cdot}015$ Å].

Apart from the intrinsic center of symmetry, the experimental geometry also exhibits a twofold axis of rotation in the oblong direction of the molecule with reasonable precision (based on bond lengths: within $2\sigma$; based on bond angles: within $5\sigma$). Both these symmetry elements are present exactly in one of the two calculated geometries, *i.e.* in the one in which the half-chair forms of the outer rings are enantiomeric (point group $2/m$). The other conformation is equally stable (energy difference 0·05 kJmol$^{-1}$) but contains homomeric half-chair forms of the outer rings (point group 222). Fig. 2 also reveals the generally good correspondence between the experimental values of the internal coordinates and the estimates from the molecular-mechanics calculation. Both bond lengths between the saturated C atoms are calculated too long. The most serious differences occur for the bond angle at C(1) (difference 1·9°) and for the out-of-plane bending of the α-methylene groups (difference 1·0°). Using an extension of the *MM*2 force field (Beckhaus, 1983) the bond-angle difference at C(1) decreases to 0·9°, but the difference in the out-of-plane bending of the α-methylene groups increases to 3·2° at the same time. Neither force field seems to be parameterized adequately at these points.

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and* $U_{eq}$ *values* ($\times 10^4$) *with their e.s.d.'s in parentheses*

$U_{\text{iso}}(\times 10^4)$ for all H atoms is fixed at 190 Å$^2$.
$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 1080 (1) | 1494 (1) | 133 (1) | 124 (2) |
| C(2) | 1620 (1) | −194 (1) | 1120 (1) | 116 (2) |
| C(3) | 3379 (1) | −364 (2) | 2283 (1) | 146 (2) |
| C(4) | 3691 (1) | −1923 (2) | 3570 (1) | 162 (3) |
| C(5) | 2813 (1) | −3912 (2) | 2854 (1) | 163 (3) |
| C(6) | 1000 (1) | −3552 (2) | 2059 (1) | 148 (2) |
| C(7) | 516 (1) | −1723 (1) | 986 (1) | 117 (1) |
| H(11) | 183 (2) | 257 (2) | 21 (2) | |
| H(31) | 398 (2) | −77 (2) | 170 (2) | |
| H(32) | 379 (2) | 102 (2) | 274 (2) | |
| H(41) | 483 (2) | −213 (2) | 418 (2) | |
| H(42) | 333 (2) | −139 (2) | 436 (2) | |
| H(51) | 312 (2) | −443 (2) | 202 (2) | |
| H(52) | 311 (2) | −498 (2) | 366 (2) | |
| H(61) | 42 (2) | −476 (2) | 147 (2) | |
| H(62) | 67 (2) | −333 (2) | 290 (2) | |

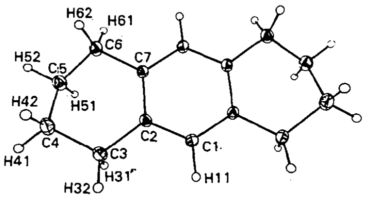

Fig. 1. *ORTEP* plot (Johnson, 1965) of 1,2,3,4,5,6,7,8-octahydroanthracene showing our numbering of the atoms. Boundary surfaces for C are drawn at the 50% probability level and for H arbitrarily.

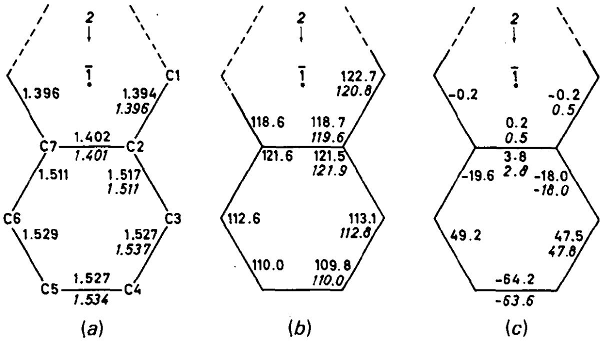

Fig. 2. Comparison of (*a*) bond lengths (Å), (*b*) bond angles (°), and (*c*) torsion angles (°) involving the heavy atoms as obtained by X-ray analysis (point group $\bar{1}$) and by empirical force-field calculations on a geometry converging to point group $2/m$ (values in italics, the direction of the twofold axis is indicated). Averaged e.s.d.'s are 0·0015 Å for bond lengths, 0·088° for bond angles and somewhat larger for torsion angles.

A search in the structural data retrieved from the Cambridge Structural Database (Allen *et al.,* 1979) for 3,4,5,6-unsubstituted cyclohexene fragments yielded 20 hits. Four entries show disorder with respect to both possible half-chair conformations of the cyclohexene ring (Aleksandrov, Shcherbakov, Struchkov & Kharchenko, 1980; Chin & Bau, 1973; Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, 1978; Kirfel, 1975). A fifth entry (Bideau & Artaud, 1970) shows an exceptionally short C(4)—C(5) single-bond length (1·412 Å) which might be caused by neglecting disorder. In the low-temperature structure of (I) no such disorder was observed although the second conformation has about the same energy. However, a martensite-type phase transition has been observed in (I) at 318K (Vatulev & Prikhot'ko, 1965) which might be connected with changes in the half-chair conformations. It is planned to continue the investigation on this point.

We thank Dr D. Tavernier (University of Gent, Belgium) for a generous gift of the title compound.

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# Structure of 8β-Bromo-6,7-didehydro-4,5α-epoxy-3-methoxy-17-methylmorphinan, $C_{18}H_{20}BrNO_2$

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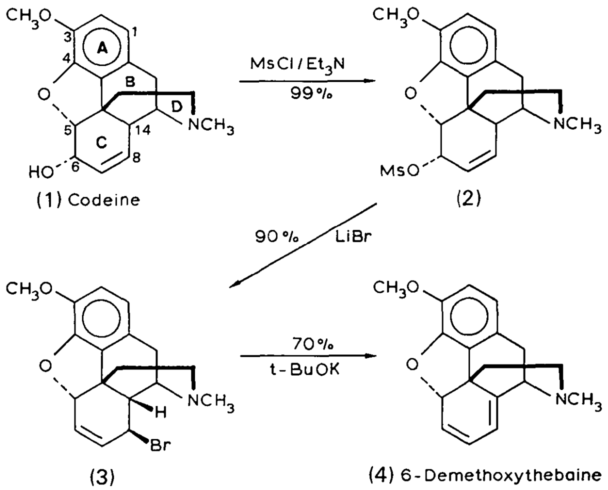
**Abstract.** $M_r = 362\cdot27$, monoclinic, $C2$, $a = 15\cdot284\,(4)$, $b = 7\cdot999\,(3)$, $c = 15\cdot493\,(4)$ Å, $\beta = 124\cdot53\,(2)^\circ$, $V = 1560\cdot5$ Å$^3$, $Z = 4$, $D_x = 1\cdot55$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot80$ mm$^{-1}$, $F(000) = 744$, $T = 298$ K. Final $R = 0\cdot062$ for 1076 observed data. The Br atom is in the 8β-position of the morphinan skeleton.

**Introduction.** Conversions of the opium alkaloid (−)-codeine (1) have been investigated to prepare (−)-6-demethoxythebaine (4) (Beyerman, Crabbendam, Lie & Maat, 1984). The latter compound plays an important role in the synthesis of etorphine-like Diels–Alder adducts of morphinan-6,8-dienes with a relatively small number of oxygen-containing substituents. So far, the only simple preparation of (4) starts from the difficultly accessible (−)-neopine, a minor alkaloid from opium (Crabbendam, Maat & Beyerman, 1981).

(−)-Codeine was converted quantitatively into 6-*O*-mesylcodeine (2) with mesyl chloride (methanesulfonyl chloride) in the presence of triethylamine. Treatment of the mesyl ester with lithium bromide in toluene and some dimethylformamide produced allylic rearrangement, affording in 90% yield (+)-8β-bromo-6,7-didehydro-4,5α-epoxy-3-methoxy-17-methylmorphinan (3). This compound can be converted easily into (4).

The assignment of the structure (3), especially regarding the position of the Br atom, remained doubtful from NMR data. Therefore, a single-crystal X-ray analysis was started, which confirmed structure (3) for the compound obtained from (−)-codeine.



**Experimental.** Title compound prepared in the Laboratory of Organic Chemistry starting from natural (−)-codeine and purified by crystallization from ethanol/diethyl ether; colorless crystals grown from acetone, m.p. 432–434 K, $[\alpha]_D^{25\cdot0\,^\circ\mathrm{C}} = +47\cdot6^\circ$ [chloroform/ethanol 9:1, 1·4 g dm$^{-3}$], irregular shape, max. edge ~0·5 mm. Systematic absences $hkl$ for $(h + k)$ odd indicated space group $Cm$ or $C2$, latter chosen on basis of distribution of peaks in Patterson function. Cell parameters obtained from diffractometer angular settings of 25 centered reflections ($9 < \theta < 18^\circ$). 1484 independent $hk\pm l$ with $2 < \theta \leq 25^\circ$ ($h_{\max}$ 18, $k_{\max}$ 9, $l \pm 18$); CAD-4 diffractometer

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