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The Low-Temperature Structure of *cis-cisoid-cis*-Perhydroanthracene, $C_{14}H_{24}$

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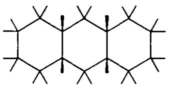
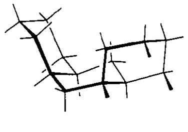
Abstract. $M_r = 192{\cdot}3$, triclinic, $P\overline{1}$, $a = 6{\cdot}491\,(2)$, $b = 9{\cdot}442\,(2)$, $c = 9{\cdot}760\,(4)$ Å, $\alpha = 107{\cdot}52\,(3)$, $\beta = 94{\cdot}37\,(3)$, $\gamma = 82{\cdot}89\,(2)°$, $V = 565{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}12$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}085$ mm^{-1}, $F(000) = 212$, $T \simeq 110$ K, final $R = 0{\cdot}041$ for 3150 (out of 3913) observed data. The bond distances, bond angles and torsion angles of the C skeleton are compared to the estimates from a molecular-mechanics calculation using the MM2 empirical force field. The favourable triple-chair form is present in the crystal, but the predicted intramolecular mirror plane shows up only approximately. The short C···C intramolecular distance between the *syn*-axial methylene groups across the central ring (3·396 Å) causes serious deformations of some of the bond and torsion angles. The distance itself is 0·13 Å shorter than predicted.

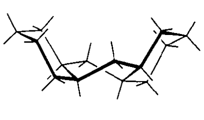
Introduction. A molecular-mechanics study on *cis-cisoid-cis*-perhydroanthracene (I) revealed that the triple-chair form (I*a*) (point group *m*) is more stable than the inverted chair-twist-chair form (I*b*) (point group 2) (Vanhee, van de Graaf, Tavernier & Baas, 1983). However, the energy difference between (I*a*) and (I*b*) is small ($\simeq 10$ kJ mol^{-1}). The triple-chair conformation is destabilized by unfavourable non-bonded interactions across the central ring between the *syn*-axial methylene groups 1 and 8. Therefore, it seemed worthwhile to determine the actual geometry in the crystal and to compare the values of bond distances, bond angles, torsion angles and non-bonded distances with the estimates for these internal coordinates from the empirical force field (EFF) calculation.



(I)



(I*a*)



(I*b*)

Experimental. Title compound (I) prepared by hydrogenation of anthracene (Fries & Schilling, 1932), m.p. 334 K, and recrystallized from acetone. Crystal $0{\cdot}40 \times 0{\cdot}35 \times 0{\cdot}30$ mm enclosed in a thin-walled capillary and cooled to 110 (2) K by a stream of cold N_2 gas. Unit-cell parameters obtained from the diffractometer angular settings of 25 reflections ($10 < \theta < 20°$). Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta_{\max} = 32{\cdot}0°$ (h: 0 to 9, k: -13 to 13, l: -14 to 14), $\omega/2\theta$-scan, scan width $(1{\cdot}20 + 0{\cdot}35 \,\text{tg}\, \theta)°$. 3913 independent reflections measured, 3155 with $I \geq 1{\cdot}0\sigma(I)$. Three reference reflections measured every hour, variation < 5%; no decay. Lorentz and polarization corrections (but none for extinction or absorption) applied. Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) yielded part of the molecule (eight C atoms); extension to the whole molecule resulted in a double solution. Proper atomic positions obtained by shifting the molecule over half a C–C bond distance. Refinement on F by full-matrix least squares. H atoms located from a difference map. Refined parameters included x, y, z of all atoms, anisotropic thermal parameters for the C atoms and isotropic thermal parameters for the H atoms. Five reflections with high F_c/F_o ratios, possibly due to extinction, removed. Final $wR = 0{\cdot}041$, $w = 1$; $S = 0{\cdot}94$, $(\Delta/\sigma)_{\max} = 0{\cdot}05$. Final difference map showed peaks of about $0{\cdot}40$ e Å^{-3} between bonded C atoms. Scattering factors for C atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965). Calculations performed on the Delft University Amdahl 470/V7B computer with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *DELPHI* (van de Graaf, Baas & van Veen, 1980; van de Graaf & Baas, 1984) using the empirical force field MM2 (Allinger, 1977).

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Table 1. *Final positional (fractional,* $\times 10^4$ *for* C; $\times 10^3$ *for* H) *and isotropic thermal parameters* ($U_{eq} \times 10^4$ Å^2 *for* C; $U_{iso} \times 10^3$ Å^2 *for* H) *with e.s.d.'s in parentheses*

	x	y	z	U^{*}_{eq}/U_{iso}
C(1)	5809 (2)	2072 (1)	999 (1)	125 (4)
C(2)	6343 (2)	2885 (1)	·41 (1)	157 (4)
C(3)	8022 (2)	3913 (1)	644 (1)	161 (4)
C(4)	9957 (2)	3028 (1)	1082 (1)	147 (4)
C(4a)	9511 (2)	2102 (1)	2056 (1)	119 (4)
C(5)	8608 (2)	2922 (1)	6154 (1)	142 (4)
C(6)	6462 (2)	3780 (1)	6469 (1)	139 (4)
C(7)	4773 (2)	2728 (1)	5948 (1)	158 (4)
C(8)	4933 (2)	1935 (1)	4341 (1)	138 (4)
C(8a)	7076 (2)	1062 (1)	3988 (1)	123 (4)
C(9)	7305 (2)	209 (1)	2387 (1)	137 (4)
C(9a)	7724 (2)	1141 (1)	1408 (1)	112 (4)
C(10)	9096 (2)	3044 (1)	3610 (1)	119 (4)
C(10a)	8855 (2)	2050 (1)	4560 (1)	117 (4)
H(11)	522 (2)	287 (2)	184 (2)	15 (4)
H(12)	475 (2)	139 (2)	55 (2)	22 (4)
H(21)	509 (2)	346 (2)	−34 (2)	16 (4)
H(22)	686 (3)	210 (2)	−94 (2)	22 (4)
H(31)	832 (2)	444 (2)	−3 (2)	19 (4)
H(32)	745 (2)	474 (2)	151 (2)	20 (4)
H(41)	1097 (2)	373 (2)	156 (2)	21 (4)
H(42)	1058 (3)	231 (2)	19 (2)	25 (4)
H(41a)	1076 (2)	139 (2)	211 (2)	12 (3)
H(51)	967 (2)	363 (2)	649 (2)	21 (4)
H(52)	885 (2)	223 (2)	672 (2)	17 (4)
H(61)	623 (2)	455 (2)	601 (2)	11 (3)
H(62)	637 (3)	428 (2)	750 (2)	23 (4)
H(71)	338 (2)	333 (2)	613 (2)	18 (4)
H(72)	499 (2)	197 (2)	648 (2)	17 (4)
H(81)	464 (2)	266 (2)	383 (2)	12 (3)
H(82)	389 (3)	120 (2)	397 (2)	21 (4)
H(81a)	724 (2)	31 (2)	450 (2)	15 (4)
H(91)	846 (2)	−57 (2)	232 (2)	12 (3)
H(92)	606 (3)	−34 (2)	201 (2)	23 (4)
H(91a)	822 (2)	40 (2)	50 (2)	19 (4)
H(101)	786 (2)	377 (2)	364 (2)	11 (3)
H(102)	1027 (3)	365 (2)	403 (2)	23 (4)
H(101a)	1013 (2)	135 (2)	451 (2)	12 (3)

* $U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *involving non-hydrogen atoms and their estimates from EFF calculation* (*MM2 force field*)

E.s.d.'s for distances and angles are in parentheses; e.s.d.'s for torsion angles are about 0·1°.

	X-ray	EFF	X-ray	
C(1)–C(2)	1·526 (2)	1·535	1·527 (2)	C(7)–C(8)
C(1)–C(9a)	1·531 (2)	1·539	1·533 (2)	C(8)–C(8a)
C(2)–C(3)	1·529 (2)	1·534	1·526 (2)	C(6)–C(7)
C(3)–C(4)	1·527 (2)	1·534	1·526 (2)	C(5)–C(6)
C(4)–C(4a)	1·535 (2)	1·540	1·535 (2)	C(5)–C(10a)
C(4a)–C(9a)	1·541 (2)	1·540	1·540 (2)	C(8a)–C(10a)
C(4a)–C(10)	1·534 (1)	1·539	1·533 (2)	C(10)–C(10a)
C(9)–C(9a)	1·538 (2)	1·543	1·536 (2)	C(8a)–C(9)
C(2)–C(1)–C(9a)	111·22 (9)	111·6	111·71 (8)	C(7)–C(8)–C(8a)
C(1)–C(2)–C(3)	110·02 (9)	110·2	110·2 (1)	C(6)–C(7)–C(8)
C(2)–C(3)–C(4)	110·7 (1)	110·4	110·52 (9)	C(5)–C(6)–C(7)
C(3)–C(4)–C(4a)	113·6 (1)	113·1	113·23 (8)	C(6)–C(5)–C(10a)
C(4)–C(4a)–C(9a)	111·05 (9)	111·6	110·97 (9)	C(5)–C(10a)–C(8a)
C(4)–C(4a)–C(10)	113·44 (9)	113·1	113·45 (9)	C(5)–C(10a)–C(10)
C(9a)–C(4a)–C(10)	110·99 (9)	111·3	111·58 (9)	C(8a)–C(10a)–C(10)
C(1)–C(9a)–C(4a)	111·71 (9)	112·6	112·25 (8)	C(8)–C(8a)–C(10a)
C(1)–C(9a)–C(9)	114·82 (9)	114·1	113·87 (9)	C(8)–C(8a)–C(9)
C(4a)–C(9a)–C(9)	110·54 (9)	111·3	110·92 (9)	C(10a)–C(8a)–C(9)
C(8a)–C(9)–C(9a)	116·12 (9)	116·9		
C(4a)–C(10)–C(10a)	111·05 (9)	110·5		
C(9a)–C(1)–C(2)–C(3)	−59·1	−57·5	57·6	C(8a)–C(8)–C(7)–C(6)
C(1)–C(2)–C(3)–C(4)	57·3	58·2	−57·7	C(8)–C(7)–C(6)–C(5)
C(2)–C(3)–C(4)–C(4a)	−54·2	−55·7	55·7	C(7)–C(6)–C(5)–C(10a)
C(3)–C(4)–C(4a)–C(9a)	50·8	51·1	−51·7	C(6)–C(5)–C(10a)–C(8a)
C(4)–C(4a)–C(9a)–C(1)	−51·3	−49·4	50·4	C(5)–C(10a)–C(8a)–C(8)
C(4a)–C(9a)–C(1)–C(2)	56·4	53·5	−54·3	C(10a)–C(8a)–C(8)–C(7)
C(4a)–C(9a)–C(9)–C(8a)	49·2	45·4	−48·2	C(10a)–C(8a)–C(9)–C(9a)
C(9)–C(9a)–C(4a)–C(10)	−53·3	−51·5	51·5	C(10)–C(10a)–C(8a)–C(9)
C(9a)–C(4a)–C(10)–C(10a)	59·2	60·0	−58·3	C(4a)–C(10)–C(10a)–C(8a)

Discussion. Positional and thermal parameters of the atoms are given in Table 1.[*] An *ORTEP* drawing (Johnson, 1965) of the molecule including the numbering of the atoms is given in Fig. 1. The C—H bond distances (e.s.d. 0·02 Å) range from 0·96–1·02 Å with an average value of 0·99 Å. The range [mean] of the C—C—H (e.s.d. 1°) and H—C—H (e.s.d. 1°) angles is 105–113° [109°] and 105–112° [107°], respectively.

Comparison between the observed and calculated geometry is restricted to the C skeleton because of the discrepancy in defining C—H bond lengths in X-ray analysis and in EFF calculations respectively.

The molecule adopts a triple-chair conformation, but the mirror plane through C(9) and C(10), predicted by the EFF calculation, is not present. In Table 2 a comparison is made between the experimental values of the internal coordinates and the estimated values using the MM2 force field; the coordinates are arranged as if the mirror plane were present.

The bond distances (Table 2) are 0·005 to 0·008 Å shorter than predicted, except for both bonds between tertiary centres. The stretching of bonds 9–9a and 9–8a (compared to 10–4a and 10–10a) under the influence of the *syn*-axial interaction between the methylene groups 1 and 8 is only very minor. However, this unfavourable interaction is clearly reflected in the large value of the valency angle at C(9) (Table 2) and the flattening of the central ring along 9–9a (9–8a) and 9a–4a (8a–10a) (Table 2). The correspondence between the experimental values of the valency angles and the corresponding values predicted by the EFF calculation is good; a difference of only 0·8° is found for the strongly deformed valency angle at C(9). The greatest discrepancy between calculated and observed values of torsion angles is found for C(4a)—C(9a)—C(9)—C(8a) and C(10a)—C(8a)—C(9)—C(9a) which both include the valency angle at C(9).

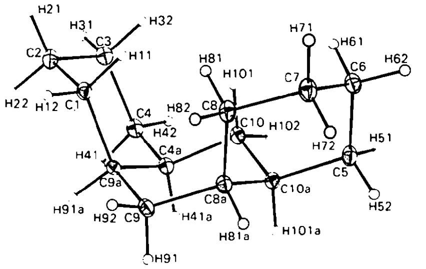

Fig. 1. The molecular structure and atom numbering of (I). Boundary surfaces for C are drawn at the 50% probability level and for H arbitrarily.

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[*] Lists of structure factors, anisotropic thermal parameters, C—H bond distances, and C—C—H and H—C—H bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39456 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The torsion angles most clearly illustrate the absence of an intramolecular mirror plane.

The observed value of the distance between the atoms C(1) and C(8) is 3·396 Å. The EFF calculated value is 3·525 Å. When the C(1)···C(8) distance and the valency angle at C(9) are constrained to the observed values during the EFF calculation, the energy rises 1·4 kJ mol^{-1} and m shows up again. An alternate empirical force field (EAS, Engler, Andose & von R. Schleyer, 1973) gives 3·602 Å for the non-bonded distance C(1)···C(8), 117·4° for the valency angle at C(9) and the energy increases by 3·3 kJ mol^{-1} when the observed values are used. Therefore, the prediction of geometric details of the strained structure of (I) using MM2 is better than with EAS. However, the former set of force-field parameters is also capable of improvement.

The crystals were provided by Dr D. Tavernier, State University at Gent, Belgium.

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Dimeric *tert*-Butylaminoboron Difluoride, $[(CH_3)_3CNHBF_2]_2$

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Abstract. $M_r = 241{\cdot}88$, orthorhombic, space group *Pbca*, $a = 7{\cdot}615\,(4)$, $b = 17{\cdot}007\,(8)$, $c = 9{\cdot}706\,(5)$ Å, $V = 1257\,(1)$ Å^3, $Z = 4$ (dimers), $D_x = 1{\cdot}278\,(1)$ g cm^{-3}, $F(000) = 512$, room temperature, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 1{\cdot}1$ cm^{-1}, $R = 0{\cdot}037$ for 776 unique observed reflections. The dimers possess crystallographic inversion symmetry, with B—N 1·595 (4) Å, and B—F 1·355 (4) and 1·366 (4) Å. The B_2N_2 rings are exactly planar.

Introduction. The dehydrohalogenation of the title compound (1) (Elter, Glemser & Herzog, 1971; Greenwood, Hooton & Walker, 1966; Greenwood & Robinson, 1968) leads to (amongst other, non-cyclic, products) the tetrameric azaborane $[(CH_3)_3CNBF]_4$ (Elter, Noltemeyer & Sheldrick, 1984). We were therefore interested to discover whether (1) already contained the eight-membered BN ring in the solid state, or if, similarly to compounds R_2NBX_2 [R = Me, X = F, Hazell (1966); R = Et, X = F, Edwards & Stadler (1970); R = Me, X = Cl, Hess (1963)], it was dimeric. The molecular weight in solution suggests a dimeric formulation, although a tetramer gradually forms on standing (Greenwood *et al.*, 1966).

Experimental. D_m not determined. Colourless rhombic prisms, sealed in glass capillaries to prevent slow hydrolysis by atmospheric moisture. Stoe two-circle diffractometer, monochromated Mo $K\alpha$ radiation. Crystal 1, mounted about **c**, 0·45 × 0·4 × 0·2 mm, layers 0–7, 1029 reflections. Crystal 2, mounted about **a**, 0·55 × 0·45 × 0·3 mm, layers 0–7, 1495 reflections. Interlayer scale factors derived from least-squares analysis of common reflections after Lp corrections. No absorption correction. 870 unique reflections (R_{int} 0·023, $2\theta_{\max}$ 55°), of which 776 with $F > 4\sigma(F)$ used for all calculations. Cell constants refined from ω values of 231 strong reflections from various positive and negative layers (Clegg & Sheldrick, 1984). Structure solution by routine direct methods. Refinement on F to R 0·037, R_w 0·036 [non-H atoms anisotropic, H(1) refining freely isotropic, other H using riding model

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