Structure of *cis*-9,10-Dibenzyl-9,10-dihydroanthracene at 193 K

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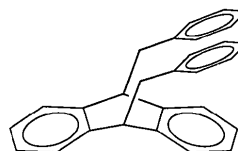
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Abstract. $C_{28}H_{24}$ (1), $M_r = 360 \cdot 5$, orthorhombic, *Pbca*, $a = 6 \cdot 694$ (1), $b = 17 \cdot 498$ (1), $c = 34 \cdot 959$ (5) Å, $V = 4094 \cdot 7$ (9) Å^3, $Z = 8$, $D_x = 1 \cdot 169$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0 \cdot 71069$ Å), $\mu = 0 \cdot 61$ cm^{-1}, $F(000) = 1536$, $T = 193$ K, $R = 0 \cdot 0402$ and $wR = 0 \cdot 0413$ for 2325 reflections [$I \geq 2\sigma(I)$]. Compound (1) has an approximate molecular mirror plane perpendicular to the anthraceno phenyl rings and bisecting C(2)—C(3) and C(6)—C(7) bonds. This symmetry can also be seen from the torsion angles C(12)—C(11)···C(11′)—C(12′) = $-2 \cdot 5$ (2)° and C(11)—C(10)···C(9)—C(11′) = $-1 \cdot 2$ (2)°. The dihedral angle between the C(1) and the C(5) phenyl rings, 148·1 (2)°, is considerably larger than the 135·2 (3)° in its counterpart, 9,10-dihydro-10,9-propenoanthracene, recently studied in our laboratory. Flattening of the anthraceno unit is a result of the presence of the bulky benzyl groups at the 9 and 10 positions. The planes of the C(9) and the C(10) benzyl groups make equal angles with the C(1) phenyl ring [39·1 (2) and 38·1 (2)°, respectively] and an angle of 22·1 (2)° with each other.

Experimental. In continuation of our work on Friedel–Crafts intramolecular cyclialkylation reactions using an AlCl$_3$ catalyst, we wanted to study the reaction of *cis*-9,10-dibenzyl-9,10-dihydroanthracene. Dihydroanthracene was dibenzylated using *n*-butyllithium and ammonia to obtain a product which had a melting-point range of 390–392 K (1). The crystal used in the X-ray analysis was obtained by slow evaporation from a benzene solution and was a pale yellow block of dimensions $0 \cdot 21 \times 0 \cdot 30 \times 0 \cdot 55$ mm. Data were collected on a Siemens *R3m/V* diffractometer equipped with a graphite monochromator utilizing Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å) and an LT-2 low-temperature delivery system (193 K). 50 reflections with $17 \cdot 89 \leq 2\theta \leq 23 \cdot 74°$ were used to refine the cell parameters. 8188 reflections were collected using the ω-scan method (h, 0→7; k, 0→20; l, −41→41), 3617 unique reflections, $R_{int} = 0 \cdot 0166$; 2θ range 3→50°, 1·2° ω scan at 4–8° min^{-1}, depending upon intensity. Four reflections ($0\overline{2}4$, $1\overline{1}1$, 111, $\overline{1}4\overline{1}$) were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was $< 1 \cdot 01\%$). Absorption corrections were applied

based on measured crystal faces using *SHELXTL-Plus* (Sheldrick, 1987); min. and max. transmission 0·9805 and 0·9973.

(1)

The structure was solved by direct methods in *SHELXTL-Plus* from which the locations of all non-H atoms were obtained. The structure was refined (*SHELX*76; Sheldrick, 1976) using full-matrix least squares and the positions of all H atoms were determined from a difference Fourier map. The

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* (Å$^2 \times 10^3$)

	x	y	z	U_{eq}*
C(1)	−10 (3)	−155 (1)	589 (1)	39 (1)
C(2)	317 (3)	−917 (1)	513 (1)	45 (1)
C(3)	339 (3)	−1439 (1)	809 (1)	46 (1)
C(4)	52 (3)	−1191 (1)	1179 (1)	41 (1)
C(4A)	−255 (3)	−418 (1)	1262 (1)	32 (1)
C(5)	−2965 (3)	678 (1)	2022 (1)	42 (1)
C(6)	−4193 (4)	1307 (1)	2049 (1)	46 (1)
C(7)	−4322 (3)	1816 (1)	1747 (1)	45 (1)
C(8)	−3190 (3)	1691 (1)	1422 (1)	38 (1)
C(8A)	−1915 (3)	1064 (1)	1393 (1)	32 (1)
C(9)	−660 (3)	947 (1)	1040 (1)	32 (1)
C(9A)	−299 (3)	106 (1)	962 (1)	31 (1)
C(10)	−528 (3)	−160 (1)	1672 (1)	35 (1)
C(10A)	−1821 (3)	545 (1)	1696 (1)	33 (1)
C(11)	1497 (4)	−37 (1)	1882 (1)	41 (1)
C(11′)	1325 (3)	1409 (1)	1071 (1)	38 (1)
C(12)	2665 (3)	−764 (1)	1926 (1)	35 (1)
C(12′)	2535 (3)	1396 (1)	707 (1)	35 (1)
C(13)	2154 (3)	−1288 (1)	2208 (1)	38 (1)
C(13′)	2058 (3)	1892 (1)	411 (1)	41 (1)
C(14)	3094 (3)	−1992 (1)	2231 (1)	43 (1)
C(14′)	3074 (4)	1872 (2)	68 (1)	53 (1)
C(15)	4568 (4)	−2183 (1)	1972 (1)	47 (1)
C(15′)	4582 (4)	1349 (2)	13 (1)	57 (1)
C(16)	5127 (3)	−1664 (1)	1697 (1)	49 (1)
C(16′)	5081 (4)	853 (2)	303 (1)	54 (1)
C(17)	4190 (3)	−961 (1)	1675 (1)	47 (1)
C(17′)	4070 (3)	880 (1)	651 (1)	45 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°) *of the non-*H *atoms*

C(1)—C(2)	1·378 (3)	C(1)—C(9A)	1·395 (3)
C(2)—C(3)	1·379 (3)	C(3)—C(4)	1·380 (3)
C(4)—C(4A)	1·397 (3)	C(4A)—C(9A)	1·394 (3)
C(4A)—C(10)	1·514 (3)	C(5)—C(6)	1·377 (3)
C(5)—C(10A)	1·392 (3)	C(6)—C(7)	1·383 (3)
C(7)—C(8)	1·385 (3)	C(8)—C(8A)	1·394 (3)
C(8A)—C(9)	1·509 (3)	C(8A)—C(10A)	1·395 (3)
C(9)—C(9A)	1·515 (3)	C(9)—C(11')	1·559 (3)
C(10)—C(10A)	1·509 (3)	C(10)—C(11)	1·556 (3)
C(11)—C(12)	1·502 (3)	C(11')—C(12')	1·509 (3)
C(12)—C(13)	1·390 (3)	C(12)—C(17)	1·390 (3)
C(12')—C(13')	1·388 (3)	C(12')—C(17')	1·382 (3)
C(13)—C(14)	1·386 (3)	C(13')—C(14')	1·379 (3)
C(14)—C(15)	1·378 (3)	C(14')—C(15')	1·377 (4)
C(15)—C(16)	1·376 (3)	C(15')—C(16')	1·377 (4)
C(16)—C(17)	1·384 (3)	C(16')—C(17')	1·391 (3)

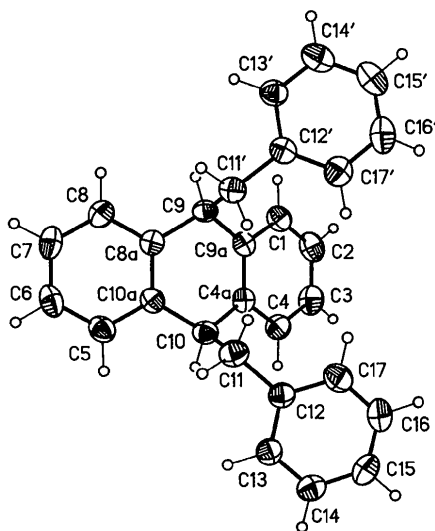|			
C(2)—C(1)—C(9A)	121·3 (2)	C(1)—C(2)—C(3)	119·9 (2)
C(2)—C(3)—C(4)	119·6 (2)	C(3)—C(4)—C(4A)	121·3 (2)
C(4)—C(4A)—C(9A)	119·0 (2)	C(4)—C(4A)—C(10)	120·1 (2)
C(9A)—C(4A)—C(10)	120·9 (2)	C(6)—C(5)—C(10A)	121·3 (2)
C(5)—C(6)—C(7)	119·9 (2)	C(6)—C(7)—C(8)	119·5 (2)
C(7)—C(8)—C(8A)	121·1 (2)	C(8)—C(8A)—C(9)	120·4 (2)
C(8)—C(8A)—C(10A)	119·1 (2)	C(9)—C(8A)—C(10A)	120·5 (2)
C(8A)—C(9)—C(9A)	111·6 (2)	C(8A)—C(9)—C(11')	110·3 (2)
C(9A)—C(9)—C(11')	112·4 (2)	C(1)—C(9A)—C(4A)	119·0 (2)
C(1)—C(9A)—C(9)	120·6 (2)	C(4A)—C(9A)—C(9)	120·4 (2)
C(4A)—C(10)—C(10A)	111·5 (2)	C(4A)—C(10)—C(11)	112·5 (2)
C(10A)—C(10)—C(11)	111·1 (2)	C(5)—C(10A)—C(8A)	119·1 (2)
C(5)—C(10A)—C(10)	119·8 (2)	C(8A)—C(10A)—C(10)	121·0 (2)
C(10)—C(11)—C(12)	112·6 (2)	C(9)—C(11')—C(12')	113·0 (2)
C(11)—C(12)—C(13)	120·3 (2)	C(11)—C(12)—C(17)	121·8 (2)
C(13)—C(12)—C(17)	117·8 (2)	C(11')—C(12')—C(13')	119·7 (2)
C(11')—C(12')—C(17')	122·0 (2)	C(13')—C(12')—C(17')	118·2 (2)
C(12)—C(13)—C(14)	121·0 (2)	C(12')—C(13')—C(14')	121·3 (2)
C(13)—C(14)—C(15)	120·2 (2)	C(13')—C(14')—C(15')	120·0 (2)
C(14)—C(15)—C(16)	119·6 (2)	C(14')—C(15')—C(16')	119·5 (2)
C(15)—C(16)—C(17)	120·2 (2)	C(15')—C(16')—C(17')	120·4 (2)
C(12)—C(17)—C(16)	121·2 (2)	C(12')—C(17')—C(16')	120·5 (2)

Fig. 1. Molecular structure of (1), with 50% probability ellipsoids, showing the atom-numbering scheme. H atoms are shown as arbitrary small circles.

non-H atoms were treated anisotropically, whereas the H atoms were refined with isotropic thermal parameters. 350 parameters were refined and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity)

$= (I_{peak} - I_{background})$(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, 0·02 is a factor used to down weight intense reflections and to account for instrument instability. An extinction correction $\chi = 0.00040$ (7) {where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$} was also applied (Sheldrick, 1987). Final $R = 0.0402$, $wR = 0.0413$ ($R_{all} = 0.0736$, $wR_{all} = 0.0488$) for 2325 reflections having $I \geq 2\sigma(I)$, and goodness of fit = 1·20. Maximum $\Delta/\sigma = 0.002$ in the final refinement cycle and the min. and max. peaks in the ΔF map were -0.16 and 0.16 e Å^{-3}, respectively. The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), while those of H atoms were from Stewart, Davidson & Simpson (1965). The positional parameters and the equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1,† bond lengths and angles in Table 2. The thermal ellipsoids drawing (*SHELXTL-Plus*, Sheldrick, 1987) of the molecule with the atom-labeling scheme is given in Fig. 1.

Related literature. Reduction of 9,10-dibenzylanthracene by lithium in liquid ammonia yields *trans*-9,10-dibenzyl-9,10-dihydroanthracene (m.p. 367 K) with a high degree of stereospecificity (Harvey, Arzadon, Grant & Urberg, 1969). On the other hand, generating the dianion of dihydroanthracene using *n*-butyllithium in ammonia and then quenching it with an excess of benzyl chloride gives *cis*-9,10-dibenzyl-9,10-dihydroanthracene (m.p. 384–385·5 K) (Harvey & Davis, 1969). The stereochemical assignments were based on chemical and proton NMR evidence. It has also been reported that 9,10-dibenzylanthracene, on reduction with sodium in pentyl alcohol, gives 9,10-dibenzyl-9,10-dihydroanthracene, having a melting point of 392 K and unknown stereochemistry (Beckwith & Waters, 1957). Also: Bass (1973); Harvey & Arzadon (1969). Related structures and Friedel–Crafts intramolecular cyclialkylation reactions: Abboud, Simonsen & Roberts (1990); Abboud, Simonsen, Tyllick & Roberts (1988); Roberts, Anderson, Khalaf & Low; (1971); Khalaf & Roberts (1972); Roberts, Bantel & Low (1973); Low & Roberts (1973); Roberts & Abdel-Baset (1976).

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Structure de la Benzoyl-6 Dihydro-2,3 Benzothiazole-1,3 One-2

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Abstract. $C_{14}H_9NO_2S$, monoclinic, $P2_1/c$, $M_r = 255 \cdot 3$, $a = 10 \cdot 924 (3)$, $b = 13 \cdot 073 (5)$, $c = 8 \cdot 269 (4)$ Å, $\beta = 95 \cdot 0 (3)°$, $V = 1176 (1)$ Å^3, $Z = 4$, $D_x = 1 \cdot 44$ Mg m^{-3}, λ(Mo $K\alpha) = 0 \cdot 7107$ Å, $\mu = 0 \cdot 22$ mm^{-1}, $F(000) = 528$, $T = 298$ K, $R = 0 \cdot 040$ for 2529 observed reflexions. Bond lengths and angles are in the usual range. The molecule is in an extended configuration, the benzene and the benzothiazol-2-one planes forming a dihedral angle of 58 (1)°. Crystal cohesion is enhanced by one hydrogen bond, between the O and the N atom of the benzothiazol-2-one moiety, forming layers. Crystal structure determination has allowed us to determine the position of the acyl group, which is in the 6 position.

Partie expérimentale. Monocristaux en forme de triangle (0,5 × 0,5 × 0,58 mm, épaisseur ≃0,05 mm), préparés par évaporation d'une solution dans l'éthanol absolu; sur diffractomètre quatre cercles Philips PW1100, monochromateur en graphite, paramètres de maille obtenus à partir de 25 réflexions (3 < θ < 7°); balayage: θ–2θ; 3799 réflexions mesurées dans l'intervalle 4 ≤ 2θ ≤ 60° avec −15 ≤ h ≤ 15, 0 ≤ k ≤ 18, 0 ≤ l ≤ 11.

Trois réflexions de contrôle (230, 112, 120) réexplorées toutes les deux heures; corrections de Lorentz–polarisation, pas de correction d'absorption, résolution par méthodes directes (*MULTAN*; Germain, Main & Woolfson, 1970); affinement sur *F* par moindres carrés sur 2529 réflexions indépendantes non nulles [$I > 3\sigma(I)$]; matrice complète anisotrope (Prewitt, 1966), H atomes localisés par synthèse de Fourier différence, affinement des positions atomiques de l'ensemble des atomes et des coefficients d'agitation thermique anisotrope, B_H fixé à 3 Å^2, $R = 0,040$ et $wR = 0,039$, avec $w = 1$; aucune réflexion rejetée; $\Delta/\sigma_{max} = 0,2$; $\Delta\rho_{max} =$