11,12-Bis(2,2-dimethylpropyl)-9,10-dihydro-9,10-ethenoanthracene

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The title compound, $C_{26}H_{32}$, was retrieved as one of three products from the reaction of *tert*-butyllithium with 11,12-dimethylene-9,10-dihydroethenoanthracene and 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane. The structure shows the expected ethenoanthracene geometry with molecules arranged *via* van der Waals surfaces.

Comment

As part of our program directed at the synthesis and study of pyramidalized alkenes, we recently investigated the dehalogenation of 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane with *t*-butyllithium in the presence of the trapping agent 11,12-dimethylene-9,10-dihydroethenoanthracene. This reaction affords small amounts of the expected Diels–Alder adduct and two additional products that result from *t*-butyllithium addition to the conjugated diene. The structure of the major product of this reaction, 11-(2,2-dimethylpropyl)-12-{2-[12-(2,2-dimethylpropyl)-9,10-ethenoanthracene-11-yl]ethyl}-9,10-dihydro-9,10-ethenoanthracene (II), has been described previously (Herres *et al.*, 2005). This investigation reports the structure of 11,12-bis(2,2-dimethylpropyl)-9,10-dihydro-9,10-ethenoanthracene, (I), which was also isolated from the reaction product mixture and crystallized from ethanol.
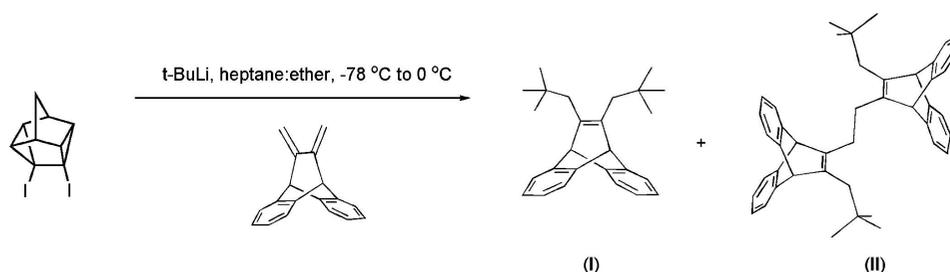
Since it is known that *t*-butyllithium reacts with conjugated dienes such as 1,3-butadiene to give neopentylallyllithium (Glaze *et al.*, 1972), the likely scenario for the formation of (I) proceeds by *t*-butyllithium addition to the conjugated diene moiety of the dimethyleneanthracene. The resulting allyllithium then undergoes lithium–iodine exchange with 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane, with subsequent coupling to a second equivalent of *t*-butyllithium.

The molecular structure (Fig. 1) of (I) shows the expected boat conformation of the central bicyclo[2.2.2]octatriene fragment. In the crystal structure, the two adjacent dimethylpropyl groups are located in positions that reduce the effects of intramolecular steric repulsion. These anticipated conformational features result in a molecular framework characterized by local pseudo-C_2 symmetry. As shown in Fig. 2, the
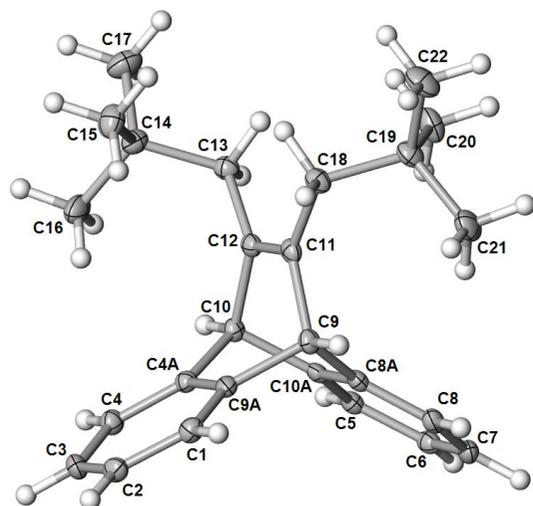
Figure 1
The molecular structure of (I), showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level.

crystal structure of (I) contains two-dimensional molecular patterns. These layers form alternating motifs with interfaces consisting of either aryl or dimethylpropyl groups with intermolecular distances larger than the sum of the van der Waals radii.

Experimental

To a solution of 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (348 mg, 0.9405 mmol) and 11,12-dimethylene-9,10-dihydroethenoanthracene (259.9 mg, 1.1286 mmol, 1.2 equivalents), in dry heptane (11.47 ml), and diethyl ether (834 µl) at 195 K was added dropwise a solution of *tert*-butyllithium in heptane (1.35 ml, 2.2 equivalents, 2.0691 mmol) under argon. The mixture was allowed to warm to 273 K, stirred at this temperature for 2 h and quenched with methanol (6 ml). Water (20 ml) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 ml), dried over Na_2SO_4 and concentrated *in vacuo*. Silica gel chromatography (gradient elution to 80:20, petroleum ether–diethyl ether) afforded pure (I). Recrystallization from absolute ethanol yielded crystals (m.p. 402–404 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (s, 18H), 2.17 (s, 4H), 4.89 (s, 2H), 6.88–6.92 (m, 4H), 7.18–7.22 (m, 4H); 13 C NMR (100.5 MHz, $CDCl_3$): δ 30.5 (CH_3), 33.3 (C), 44.6 (CH2), 57.2 (CH), 122.7 (CH), 124.1 (CH), 144.5 (C), 146.5 (C).

Crystal data

$C_{26}H_{32}$	$D_x = 1.080$ Mg m^{-3}
$M_r = 344.52$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7338
$a = 35.531$ (7) Å	reflections
$b = 12.536$ (3) Å	$\theta = 2.3–27.8°$
$c = 9.518$ (2) Å	$\mu = 0.06$ mm^{-1}
$\beta = 91.610$ (2)°	$T = 173$ (2) K
$V = 4237.7$ (15) Å^3	Plate, colorless
$Z = 8$	0.24 × 0.18 × 0.02 mm

Data collection

Bruker SMART APEX CCD	3235 reflections with $I > 2\sigma(I)$
diffractometer	$R_{int} = 0.048$
φ and ω scans	$\theta_{max} = 25.4°$
Absorption correction: none	$h = -42 \rightarrow 42$
15857 measured reflections	$k = -15 \rightarrow 15$
3878 independent reflections	$l = -11 \rightarrow 11$
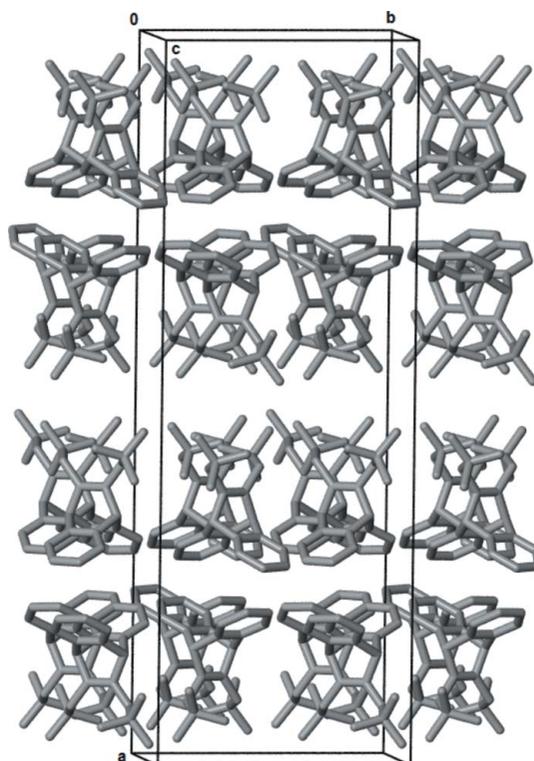
Figure 2
View of the molecular packing of (I), projected approximately down the *c* axis.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.9402P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
3878 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
241 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C4A—C9A	1.401 (2)	C10—C4A	1.5266 (19)
C8A—C10A	1.3992 (19)	C10—C12	1.5409 (19)
C9—C9A	1.5265 (19)	C11—C12	1.337 (2)
C9—C8A	1.5296 (19)	C11—C18	1.5104 (19)
C9—C11	1.544 (2)	C12—C13	1.511 (2)
C10—C10A	1.5245 (19)		
C12—C11—C18	127.32 (13)	C11—C12—C13	128.13 (13)
C12—C11—C9	113.42 (12)	C11—C12—C10	113.36 (12)
C10—C12—C13—C14	80.48 (16)	C9—C11—C18—C19	79.72 (16)
C12—C13—C14—C15	62.88 (17)	C11—C18—C19—C20	60.78 (17)

All H atoms were treated as riding with C—H distances of 0.95 (C_{Ar}H), 0.98 (CH_3), 0.99 (CH_2) and 1.00 Å (CH), and with U_{iso}(H) = 1.2U_{eq}(C) [1.5U_{eq}(C) for methyl H atoms]. Riding methyl H atoms were allowed to rotate freely during refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics:

X-SEED; software used to prepare material for publication: *X-SEED* (Barbour, 2001).

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