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

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## Key indicators

Single-crystal X-ray study  
 $T = 173\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.048  
 $wR$  factor = 0.119  
Data-to-parameter ratio = 16.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{26}\text{H}_{32}$ , 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<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonane. The structure shows the expected ethenoanthracene geometry with molecules arranged *via* van der Waals surfaces.

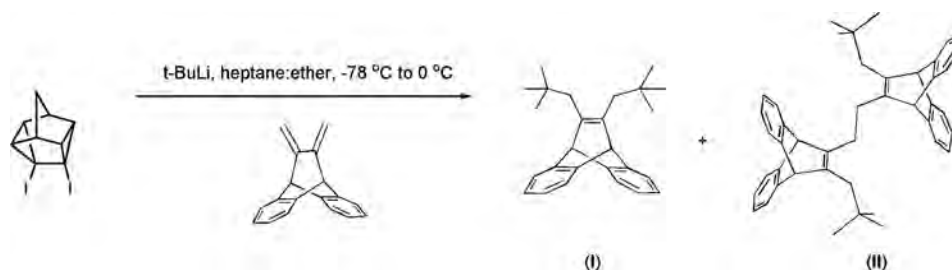
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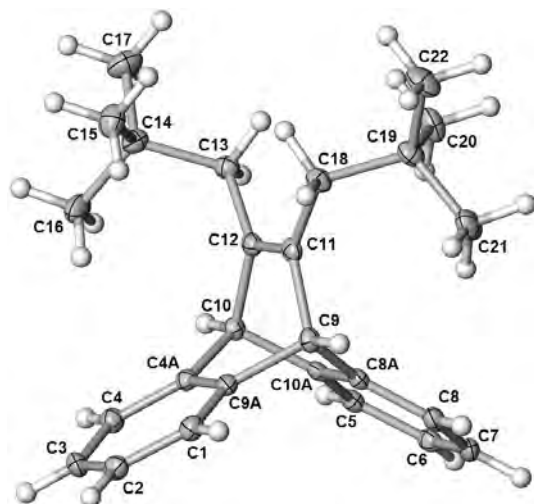
## Comment

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<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]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-(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<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]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

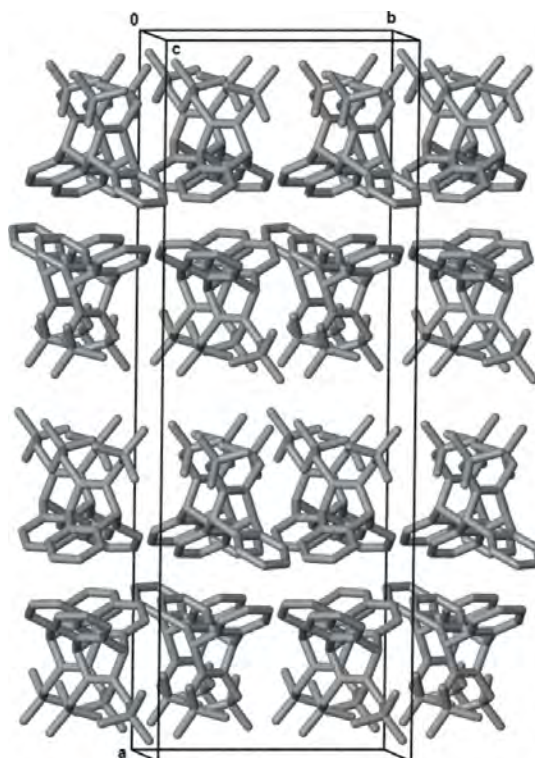
To a solution of 4,5-diiodopentacyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,8</sup>.0<sup>5,7</sup>]nonane (348 mg, 0.9405 mmol) and 11,12-dimethylene-9,10-dihydroethenoanthracene (259.9 mg, 1.1286 mmol, 1.2 equivalents), in dry heptane (11.47 ml), and diethyl ether (834  $\mu$ l) at 195 K was added dropwise 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<sub>2</sub>Cl<sub>2</sub> (3  $\times$  30 ml), dried over Na<sub>2</sub>SO<sub>4</sub> 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). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (s, 18H), 2.17 (s, 4H), 4.89 (s, 2H), 6.88–6.92 (m, 4H), 7.18–7.22 (m, 4H); <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>):  $\delta$  30.5 (CH<sub>3</sub>), 33.3 (C), 44.6 (CH<sub>2</sub>), 57.2 (CH), 122.7 (CH), 124.1 (CH), 144.5 (C), 146.5 (C).

### Crystal data

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

### Data collection

Bruker SMART APEX CCD diffractometer	3235 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.048$
Absorption correction: none	$\theta_{\text{max}} = 25.4^\circ$
15857 measured reflections	$h = -42 \rightarrow 42$
3878 independent reflections	$k = -15 \rightarrow 15$
	$l = -11 \rightarrow 11$



**Figure 2**  
View of the molecular packing of (I), projected approximately down the *c* axis.

### Refinement

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

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C4A–C9A	1.401 (2)	C10–C4A	1.5266 (19)
C8A–C10A	1.3992 (2)	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<sub>Ar</sub>H), 0.98 (CH<sub>3</sub>), 0.99 (CH<sub>2</sub>) and 1.00  $\text{\AA}$  (CH), and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{C})$  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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## References

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). *SMART* (Version 5.625) and *XPREP* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2002). *SAINT*. Version 6.36A. Bruker AXS Inc., Madison, Wisconsin, USA.
- Glaze, W. H., Hanicak, J. E., Moore, M. L. & Chaudhuri, J. (1972). *J. Organomet. Chem.* **44**, 39–48.
- Herres, J. P., Forman, M. A. & Wheeler, K. A. (2005). *Acta Cryst.* **E61**, o1223–o1225.