

11-(2,2-Dimethylpropyl)-12-[2-[12-(2,2-dimethylpropyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl]-ethyl]-9,10-dihydro-9,10-ethenoanthracene

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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.059
 wR factor = 0.134
Data-to-parameter ratio = 15.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Reaction of *tert*-butyllithium with 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene and 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane gives three products, one of which crystallizes from petroleum ether as the title compound, C₄₄H₄₆, (I). Molecules of (I) are positioned on inversion centers ($Z' = 0.5$) in the space group $P2_1/n$ and lack any discernible intermolecular interactions.

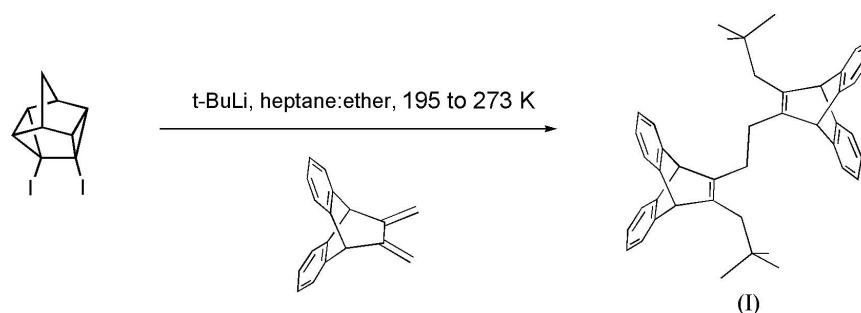
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Comment

We recently attempted dehalogenation of 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane at 273 K using *tert*-butyllithium in the presence of the trapping agent 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene. The reaction afforded three distinct compounds as indicated from GS-MS analysis. Separation of these compounds *via* column chromatography and subsequent NMR investigation suggests one of the minor components is the expected Diels-Alder adduct. The major product of the reaction mixture was isolated and crystallized from petroleum ether as 11-(2,2-dimethylpropyl)-12-[2-[12-(2,2-dimethylpropyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl]ethyl]-9,10-dihydro-9,10-ethenoanthracene, (I).



Although it is known that *tert*-butyllithium reacts with 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene at low temperature (Eaton & Lukin, 1995), the course of this reaction and product identity have yet to be reported. The current investigation seeks to characterize and understand the formation of reaction products for this process. Based on the ability of *tert*-butyllithium to react with conjugated dienes such as 1,3-butadiene to give neopentylallyllithium (Glaze *et al.*, 1972), we believe that *tert*-butyllithium adds to 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene to yield an allyllithium followed by lithium-iodine exchange with 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane. This product then couples with another molecule of the allyllithium to form (I).

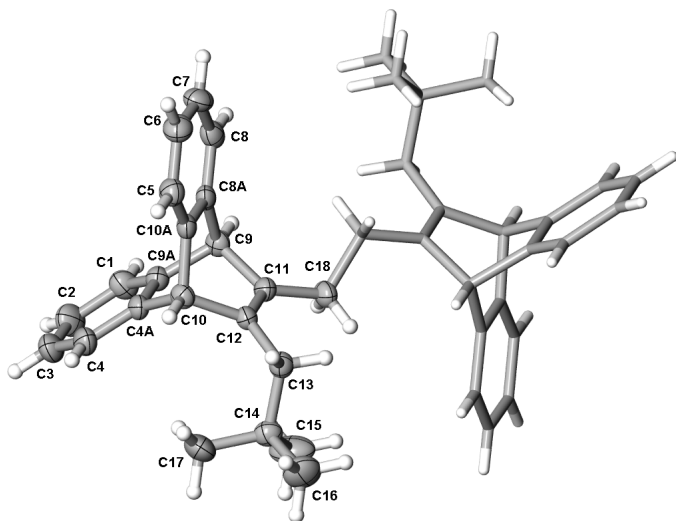


Figure 1

The molecular structure and atom-labeling scheme of (I). Unlabeled atoms are related by the symmetry code $(2-x, 1-y, -z)$. Displacement ellipsoids for the asymmetric unit are drawn at the 50% probability level.

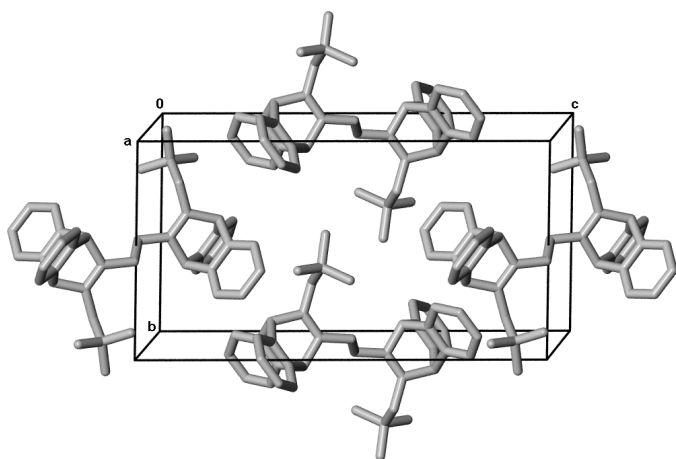


Figure 2

View of the molecular packing of (I), projected approximately down the *a* axis. H atoms have been omitted.

The asymmetric unit consists of one half-molecule of (I) positioned on an inversion center (Fig. 1). Inspection of the dihydroethanoanthracene fragment reveals the expected idealized boat conformation with a pendant orthogonally positioned $[C10-C12-C13-C14 = 87.3(3)^\circ]$ *tert*-butyl group. Fig. 2 shows the crystal structure. An interesting feature of this structure is the lack of any prominent non-bonded contacts. The absence of face-to-face $\pi-\pi$ stacking interactions and edge-to-face aromatic $C-H \cdots \pi$ interactions suggests molecules of (I) assemble by favorable organization of van der Waals surfaces.

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-dihydro-9,10-

ethanoanthracene (259.9 mg, 1.1286 mmol, 1.2 equivalents) in dry heptane (11.47 ml) and diethyl ether (0.834 ml) at 195 K was added dropwise a solution of *tert*-butyllithium in heptane (1.35 ml, 2.2 equivalents, 2.0691 mmol, 0.53 M) 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) ($R_F = 0.27$, 97:3 petroleum ether–diethyl ether), which on slow evaporation of a solution in petroleum ether yielded X-ray quality crystals (m.p. 499–500 K). 1H NMR (400 MHz, $CDCl_3$): δ 0.84 (s, 18H), 2.09 (s, 4H), 2.48 (s, 4H), 4.83 (s, 2H), 4.85 (s, 2H), 6.92 (m, 8H), 7.21 (m, 8H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 29.2 (CH_2), 30.3 (CH_3), 33.1 (C), 44.6 (CH_2), 55.4 (CH), 57.6 (CH), 122.4 (CH), 122.8 (CH), 124.3 (2CH), 124.3 (CH), 142.1 (C), 145.4 (C), 146.3 (C), 146.3 (C).

Crystal data

$C_{44}H_{46}$
 $M_r = 574.81$
 Monoclinic, $P2_1/n$
 $a = 9.2450(8) \text{ \AA}$
 $b = 10.0697(9) \text{ \AA}$
 $c = 18.870(2) \text{ \AA}$
 $\beta = 102.654(8)^\circ$
 $V = 1714.0(3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.114 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 52 reflections
 $\theta = 23.7\text{--}24.9^\circ$
 $\mu = 0.06 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Prism, colorless
 $0.44 \times 0.28 \times 0.08 \text{ mm}$

Data collection

Siemens P4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4212 measured reflections
 3136 independent reflections
 1667 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$

$\theta_{max} = 25.4^\circ$
 $h = -1 \rightarrow 11$
 $k = -1 \rightarrow 12$
 $l = -22 \rightarrow 22$
 3 standard reflections
 every 97 reflections
 intensity decay: $<3\%$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.134$
 $S = 1.00$
 3136 reflections
 202 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$

Table 1

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

C4A–C10	1.518 (3)	C9–C11	1.535 (3)
C8A–C9	1.525 (3)	C10–C10A	1.518 (3)
C9–C9A	1.523 (3)	C10–C12	1.542 (3)
C9A–C9–C8A	105.96 (18)	C4A–C10–C12	106.41 (19)
C9A–C9–C11	106.8 (2)	C10A–C10–C12	106.45 (19)
C8A–C9–C11	105.9 (2)	C12–C13–C14	117.2 (2)
C4A–C10–C10A	105.5 (2)	C11–C18–C18 ⁱ	112.5 (3)

Symmetry code: (i) $2-x, 1-y, -z$.

All H atoms were treated as riding with C–H distances of 0.93 ($C_{Ar}-H$), 0.96 (CH_3), 0.97 (CH_2) and 0.98 \AA (CH), and with $U_{iso}(H) = 1.2U_{eq}(C)$ ($1.5U_{eq}$ for methyl H atoms). Methyl groups were allowed to rotate freely during refinement.

Data collection: XSCANS (Bruker, 1999); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97* and *X-SEED*.

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