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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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Reaction of tert-butyl lithium with 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene and 4,5-diiodopentacyclo[4.3.0.0\textsuperscript{2,4}.0\textsuperscript{3,8}.0\textsuperscript{5,7}]nonane gives three products, one of which crystallizes from petroleum ether as the title compound, C\textsubscript{44}H\textsubscript{46} (I). Molecules of (I) are positioned on inversion centers (Z = 0.5) in the space group P\textsubscript{2\textsubscript{1}}/n and lack any discernible intermolecular interactions.

Comment

We recently attempted dehalogenation of 4,5-diiodopentacyclo[4.3.0.0\textsuperscript{2,4}.0\textsuperscript{3,8}.0\textsuperscript{5,7}]nonane at 273 K using tert-butyl lithium 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-[12-(2,2-dimethylpropyl)-9,10-dihydro-9,10-ethanoanthracen-11-yl]ethyl]-9,10-dihydro-9,10-ethanoanthracene, (I).

Although it is known that tert-butyl lithium 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-butyl lithium to react with conjugated dienes such as 1,3-butadiene to give neopentylallyllithium (Glaze et al., 1972), we believe that tert-butyl lithium 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\textsuperscript{2,4}.0\textsuperscript{3,8}.0\textsuperscript{5,7}]nonane. This product then couples with another molecule of the allyllithium to form (I).
idealized boat conformation with a pendant orthogonally dihydroethanoanthracene fragment reveals the expected positioned on an inversion center (Fig. 1). Inspection of the Waals surfaces. molecules of (I) assemble by favorable organization of van der Waals interactions suggests stacking interactions of this structure is the lack of any prominent non-bonded 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\( ^7 \)]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 \( CH_2Cl_2 \) (\( 3 \times 30 \) 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, \( CDCl_3 \)): \( \delta \) 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); \(^13C\) NMR (100.5 MHz, \( CDCl_3 \)): \( \delta \) 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 (C\(_2\)H), 124.3 (CH), 141.2 (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) Å

\( b = 10.0697 \) (9) Å

\( c = 18.870 \) (2) Å

\( \beta = 102.654 \) (8)°

\( V = 1714.0 \) (3) Å\(^3\)

\( D_\lambda = 1.114 \) Mg m\(^{-3}\)

Mo Kα radiation

Cell parameters from 52 \( \theta \) = 25.4°

\( h = -1 \rightarrow 11 \)

\( k = -1 \rightarrow 12 \)

\( l = -22 \rightarrow 22 \)

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

\( w = 1/\sigma^2(F^2) + (0.0526P^2) \)

where \( P = (F^2 + 2F_c^2)/3 \)

\( \Delta\rho_{max} = 0.16 \) e Å\(^{-3}\)

\( \Delta\rho_{min} = -0.17 \) e Å\(^{-3}\)

**Table 1**

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>C(<em>{4A})–C(</em>{10})</th>
<th>1.518 (3)</th>
<th>C(<em>9)–C(</em>{11})</th>
<th>1.535 (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{8A})–C(_9)</td>
<td>1.525 (3)</td>
<td>C(<em>{10})–C(</em>{10A})</td>
<td>1.518 (3)</td>
</tr>
<tr>
<td>C(<em>{9})–C(</em>{9A})</td>
<td>1.525 (3)</td>
<td>C(<em>{10})–C(</em>{12})</td>
<td>1.542 (3)</td>
</tr>
<tr>
<td>C(<em>{8A})–C(</em>{9A})–C(_{10A})</td>
<td>105.96 (18)</td>
<td>C(<em>{8A})–C(</em>{10})–C(_{12})</td>
<td>106.41 (19)</td>
</tr>
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<td></td>
<td>106.8 (2)</td>
<td>C(<em>{10})–C(</em>{10A})–C(_{12})</td>
<td>106.45 (19)</td>
</tr>
<tr>
<td></td>
<td>105.9 (2)</td>
<td>C(<em>{12})–C(</em>{13})–C(_{14})</td>
<td>117.2 (2)</td>
</tr>
<tr>
<td></td>
<td>105.5 (2)</td>
<td>C(<em>{11})–C(</em>{18})–C(_{18A})</td>
<td>112.3 (3)</td>
</tr>
</tbody>
</table>

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

All H atoms were treated as riding with C—H distances of 0.93 (C\(_{4}\)–H), 0.96 (CH\(_3\)), 0.97 (CH\(_2\)) and 0.98 Å (CH), and with \( U_{eq}(H) = 1.2U_{eq}(C) \) (1.5\( U_{eq}(C) \) 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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References