

Communication

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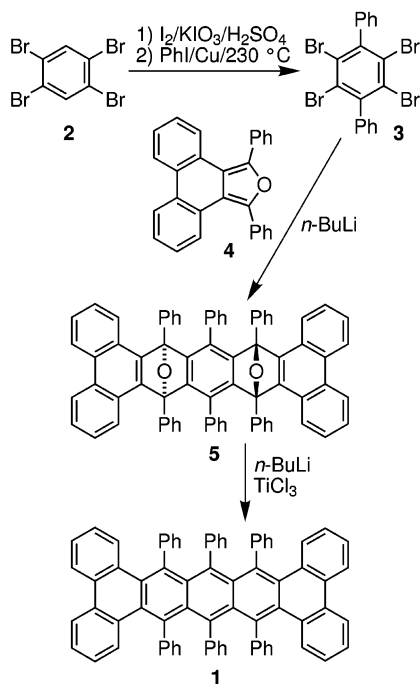
## A Pentacene with a 144° Twist

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Sterically congested polycyclic aromatic hydrocarbons (PAHs) frequently adopt twisted or helical conformations, and such molecules not only are aesthetically pleasing but also may possess unusual properties.<sup>1,2</sup> In recent years, researchers from our laboratory and others have reported the syntheses of several longitudinally twisted PAHs,<sup>3</sup> including an acene “ribbon” with an end-to-end twist of 105°,<sup>3f</sup> but the resolution of these compounds into pure enantiomers was not achieved. We report here the synthesis, molecular structure, and resolution of 9,10,11,20,21,22-hexaphenyltetrabenzo[*a,c,l,n*]pentacene (**1**), a PAH with a 144° twist—by far the most highly twisted PAH yet prepared.



The synthesis of **1** is quite short. 1,2,4,5-Tetrabromobenzene (**2**) was doubly iodinated, and a crossed Ullmann coupling reaction replaced the iodines with phenyl groups to give the terphenyl **3** in 20% yield.<sup>4</sup> The high temperature (230 °C) of the latter, classical reaction is a desirable feature when dealing with the relatively insoluble hexahalobenzene intermediate. Compound **3** is a bisaryne equivalent, and treatment of **3** with *n*-butyllithium in the presence of 1,3-diphenylphenanthro[9,10-*c*]furan<sup>5</sup> (**4**) gave the double adduct **5** in 26% yield.<sup>6</sup> The illustrated *trans* geometry was established by X-ray analysis (data not shown). The deoxygenation of similar adducts was the most difficult step in two previous twisted PAH syntheses, with yields as low as 3% in the case of

decaphenylanthracene.<sup>3e,f</sup> However, the deoxygenation of **5** by low-valent titanium (TiCl<sub>3</sub>/*n*-butyllithium<sup>7</sup>) proceeded relatively smoothly: 90% pure **1** was obtained in 51% yield, and one recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH gave homogeneous **1** in 27% yield.<sup>8</sup>

Compound **1** is a bright red solid, with a strong orange fluorescence in solution [ $\lambda_{\text{max}}(\text{CHCl}_3) = 589 \text{ nm}$ ,  $\Phi = 7.4\%$ , [Ru(bipy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> reference]. Although high-melting (mp > 470 °C), it is freely soluble in common organic solvents. Long red needles were obtained upon evaporation of benzene–ethanol solutions, but these crystals tended to be multiple. When the crystals were cut to yield more nearly single crystals, the weak data collected by using conventional X-ray sources were suitable only for a preliminary determination, but these data did establish that the molecule was strongly twisted. A better data set was obtained by using a small crystal fragment and a synchrotron X-ray source, and the resulting structure is shown in Figure 1.

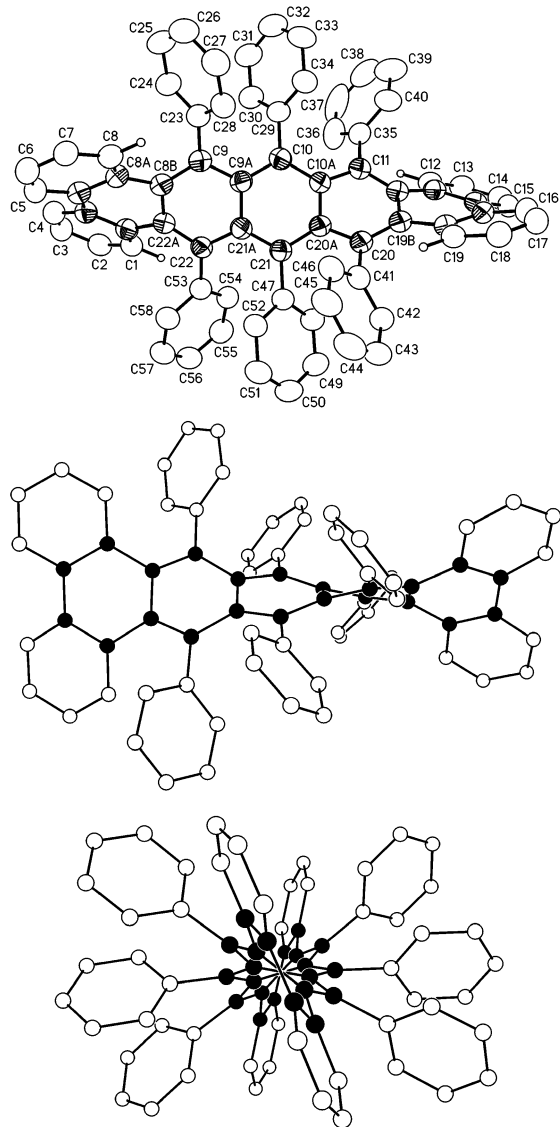
Compound **1** crystallizes in the monoclinic space group *P2*<sub>1</sub>/*c* with *Z* = 4.<sup>9</sup> The molecule lies on a general position, and it possesses approximate *D*<sub>2</sub> symmetry. The end-to-end twist<sup>3a</sup> of the pentacene nucleus in **1** is 143.6°, in excellent agreement with AM1 (143°), HF/3-21G (144°), and B3LYP/6-31G(d) (149°) calculations.<sup>13</sup> The twist is evenly distributed, with the five pentacene rings (left to right in Figure 1) contributing approximately 30°, 30°, 27°, 28°, and 27° of twist. The *ipso* carbon atoms of the phenyl substituents are forced into close contact with each other as well as with benzo hydrogens on the terminal phenanthrene groups. The four C–C contacts [e.g., C(23)–C(29)] average 2.94 Å, and the four C–H contacts [e.g., C(23)–H(8)] average 2.38 Å.<sup>14</sup> Despite its distortion from planarity, solid **1** is completely stable in air at room temperature. Solutions of **1** are stable indefinitely in the dark, but in bright room light **1** is slowly oxidized (*t*<sub>1/2</sub> ≈ 36 h) to give products of unknown structure. This stands in contrast to the much greater sensitivity of 9,11,20,22-tetraphenyltetrabenzo[*a,c,l,n*]pentacene, which, lacking the two phenyl groups on the central pentacene ring, rapidly forms a 10,22-endoperoxide in ambient light.<sup>3g</sup>

The resolution of **1** into pure enantiomers with very high optical rotations was of great interest to us. This had not proved possible with any of our previously reported twisted PAHs because their barriers to racemization ( $\Delta G^{\ddagger}_{\text{rac}}$ ) are too low. Rapid racemization is the norm because these molecules do not racemize via a single, high-energy, planar transition state, but rather through one or more nonplanar intermediates accessible by lower energy transition states.<sup>3d,g</sup> However, in the case of **1**, computational studies<sup>13</sup> at the AM1 level found a *D*<sub>2</sub>-symmetric ground state, a *C*<sub>2h</sub>-symmetric intermediate ( $\Delta E = 12.6 \text{ kcal/mol}$ ), and a *C*<sub>1</sub>-symmetric transition state linking the two ( $\Delta E = 22.5 \text{ kcal/mol}$ ). Thus, racemization would entail the sequence (+)-*D*<sub>2</sub> → *C*<sub>2h</sub> → (–)-*D*<sub>2</sub>, and the calculated barrier corresponds to a half-life of 1 h at room temperature, long enough to permit at least partial resolution. In the event, **1** was easily resolved by preparative HPLC on a Chiralcel

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**Figure 1.** Three views of the molecular structure of **1**. In the top view, thermal ellipsoids have been drawn at the 50% probability level, and the four sterically encumbered hydrogen atoms have been retained (all other hydrogen atoms have been omitted for clarity).

OD column (solvent, ethanol). The first peak to elute exhibited  $[\alpha]^{25}_D = +7440 \pm 150^\circ$  ( $c = 0.00669$ ), and the second  $[\alpha]^{25}_D = -7420 \pm 150^\circ$  ( $c = 0.00363$ ); both specific rotations were measured within a few minutes of elution. The barrier to racemization was determined by two methods: the half-life for the decay of optical rotation at  $25^\circ\text{C}$  was 9.3 h, and the half-life for the loss of enantiomeric excess (as judged by HPLC analysis) at  $27^\circ\text{C}$  was 6.2 h. Both values yield a  $\Delta G^\ddagger_{\text{rac}}$  of 23.8 kcal/mol (via the Eyring equation and assuming a transmission coefficient of 1).

It is probable that even longer, more highly twisted PAHs than **1** will be stable species, provided that the central polycycle is protected from reaction by sterically demanding groups. Such compounds should be configurationally stable and have exceptional chiroptical properties, but their synthesis remains a challenge.

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**Supporting Information Available:** Synthetic procedures and NMR spectra for **1**, **3**, and **5**; racemization data for **1**; and a crystallographic information file, in CIF format, containing the X-ray structural information for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (4) For **3**: mp  $262\text{--}265^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.15–7.26 (m, 4 H), 7.43–7.54 (m, 6 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  127.3, 128.7, 128.8, 128.9, 144.1, 146.0; MS (EI)  $m/z$  546 ( $\text{M}^+$ , 36), 386 ( $\text{M} - \text{Br}_2$ , 36), 226 ( $\text{M} - \text{Br}_4$ , 100); exact mass 545.7468, calcd for  $\text{C}_{18}\text{H}_{10}^{79}\text{Br}_2^{81}\text{Br}_2$  545.7475.
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- (6) For **5**: mp  $>470^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  6.91 (t,  $J = 8$  Hz, 8 H), 7.02 (t,  $J = 8$  Hz, 4 H), 7.10 (t,  $J = 7$  Hz, 2 H), 7.15 (d,  $J = 7$  Hz, 8 H), 7.23 (m, 8 H), 7.89 (m, 8 H), 8.20 (d,  $J = 8$  Hz, 4 H), 9.18 (d,  $J = 8$  Hz, 4 H); MS (FAB)  $m/z$  967 ( $\text{M} + \text{H}$ , 100).
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- (8) For **1**: mp  $>470^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.41 (t,  $J = 7.5$  Hz, 4 H), 6.52 (t,  $J = 7.5$  Hz, 2 H), 6.56 (dd,  $J = 8$ , 1 Hz, 4 H), 6.62–6.71 (m, 12 H), 6.75 (m, 8 H), 6.86 (tt,  $J = 7.5$ , 1 Hz, 4 H), 6.92 (td,  $J = 7.5$ , 1 Hz, 4 H), 7.23 (td,  $J = 7.5$ , 1 Hz, 4 H), 8.07 (dd,  $J = 8$ , 1 Hz, 4 H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  123.7, 125.6, 126.0, 126.5, 126.9, 128.0, 128.1, 128.3, 130.3, 132.4, 132.9, 133.2, 133.3, 133.4, 134.4, 134.5, 135.3, 140.2, 141.4 (19 of 22 expected resonances); MS (FAB)  $m/z$  934 ( $\text{M}^+$ , 100); UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 376 (4.84, sh), 393 (5.10), 482 (3.88, sh), 506 (3.97), 538 (3.86).
- (9) Crystal data for **1**:  $\text{C}_{74}\text{H}_{46}$ ,  $M = 935.11$ ; monoclinic, space group  $P2_1/c$  (No. 14);  $a = 15.5738(5)$ ,  $b = 17.2429(8)$ , and  $c = 18.2439(8)$  Å,  $\beta = 90.816(2)^\circ$ ,  $V = 4898.7(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.268$  g/cm<sup>3</sup>. Intensity data were collected at 100 K with  $\theta \leq 31.79^\circ$  and  $\lambda = 0.97791$  Å by using the National Synchrotron Light Source (beamline X29). A total of 83 784 reflections was processed by using the programs HKL-2000,<sup>10</sup> PLATON,<sup>11</sup> and SHELXTL<sup>12</sup> to give 6110 unique reflections ( $R_{\text{int}} = 0.099$ ). The structure was solved by direct methods; non-hydrogen atoms were refined anisotropically, with hydrogens riding [ $\text{C}-\text{H} = 0.95$  Å,  $U(\text{H}) = 1.2U(\text{C})$ ] (SHELXTL). The refinement converged to  $R(F) = 0.0635$ ,  $wR(F^2) = 0.1847$ , and  $S = 1.075$  for 5433 reflections with  $I > 2\sigma(I)$ , and  $R(F) = 0.0683$ ,  $wR(F^2) = 0.1937$ , and  $S = 1.056$  for 6110 unique reflections, 669 parameters, and 2 restraints.
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- (13) All calculations were performed by using GAUSSIAN 98; the built-in default thresholds for wave function and gradient convergence were employed; transition-state structures were located by using the QST3 option and verified by frequency calculations.
- (14) For estimation of nonbonded contact distances, the C–H bond distances were “improved” to 1.083 Å, the standard value observed in neutron diffraction experiments (Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19).

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