Synthesis and properties of 1,6,7,12,13,18,19,24-octamethylacenaphthyleno[*b*,*l*]tetraphenylene

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The X-ray crystal structure and photophysical properties of 1,6,7,12,13,18,19,24-octamethylacenaphthyleno[*b*,*l*]tetraphenylene, which has been synthesized *via* a Diels–Alder reaction of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene and 6,7-dihydro-6-hydroxy-7,9-dimethyl-8*H*-cyclopenta-[*a*]acenaphthylene-8-one, are reported.

Non-planar polycyclic aromatic hydrocarbons with a parabolic curvature result from perturbations caused by the incorporation of a five-membered ring into a planar graphite surface.[1] Fullerenes, buckybowls, and buckytubes are all manifestations of this effect.[2] Related perturbations, caused by the incorporation of larger rings (7 or 8 members), can be observed in the saddle-like structures of [7]circulene (**1**)[3] and dibenzo[*def*,*pqr*]tetraphenylene (**2**).[4] Herein, we report the synthesis and properties of a novel saddle-shaped tetraphenylene derivative (**3**) containing two fluoranthene subunits.
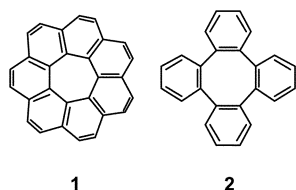

The synthesis of fluoranthene derivatives can be accomplished *via* Diels–Alder reaction between a cyclopentadienone and an acetylene (or masked acetylene).[1,5] Thus, tetraphenylene **3** can be envisioned to come from 5,6,11,12-tetradehydrodibenzo-[*a*,*e*]cyclooctene (**4**) and cyclopentadienone **5** (Scheme 1).
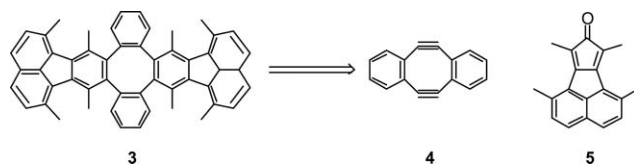
Scheme 1 Retrosynthesis of **3**.

Diyne **4** is readily prepared in high yield through a double elimination protocol recently reported by Otera and coworkers.[6] Immediately after purification, diyne **4** and the previously reported 6,7-dihydro-6-hydroxy-7,9-dimethyl-8*H*-cyclopenta[*a*]acenaphthylene-8-one (**6**)[2e] were heated to 100 °C in acetic anhydride for 12 h. Gratifyingly, the highly strained acetylenic bonds[7] of **4** reacted rapidly with cyclopentadienone **5**, formed *in situ* from **6**, to produce 1,6,7,12,13,18,19,24-
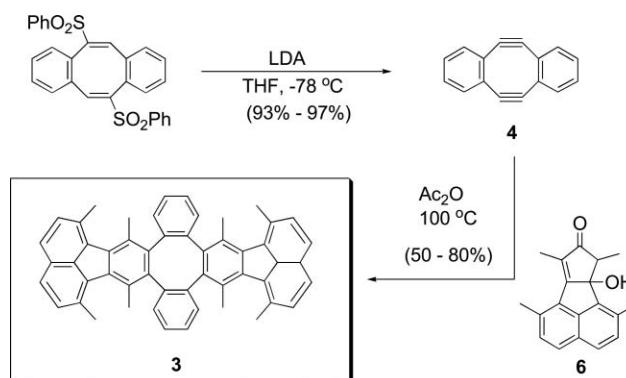
octamethyldibenzo[*def*,*pqr*]tetraphenylene (**3**) in good yield (Scheme 2).[8]

The X-ray crystal structure of **3** (Fig. 1)† reveals a C_2 symmetric molecule with a severely twisted surface. The twisting is continuous from one naphthalene subunit, through the tetraphenylene core, to the naphthalene of the other fluoranthene subunit. The angle between the mean planes of the naphthalene and benzene units is 19.55°. Although the parent fluoranthene (**7**) is flat, a similar degree of twisting is observed for the sterically similar 1,6,7,10-tetramethylfluoranthene (**8**).[9] Aside from minor twisting, the tetraphenylene core of **3** is unchanged by this perturbation. Another interesting structural feature is the proximity of the methyl groups in the 7,12,19,24-positions to the benzene protons of the tetraphenylene subunit
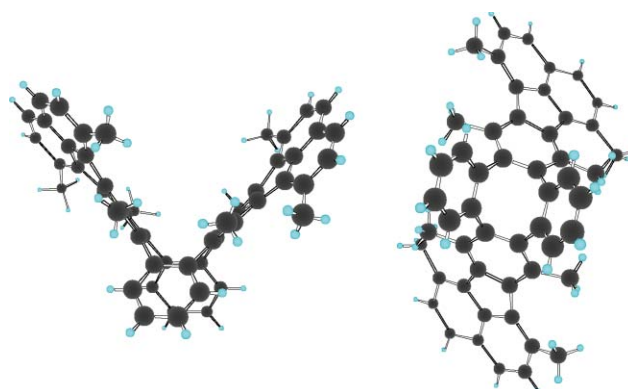

Scheme 2 Synthesis of **3**.

Fig. 1 Two perspectives of the X-ray crystal structure of **3**: (left) along C_2 axis; (right) view through cleft.†

(2.9–3.3 Å). Such an arrangement brings to mind the possibility of ring-closure of a suitable precursor to an [8]circulene type structure, with alternating six- and five-membered rings.

The distortion of **3** from D_{2h} (planar) to C_2 (ground state) gives rise to the possibility of dynamic behavior. The two possible dynamic modes of interest are the inversion of the core eight-membered ring through the plane and the twisting of the fluoranthene subunit. The former process is highly unlikely at room temperature, for example, an exceptional thermal racemization barrier of 67.2 ± 0.8 kcal mol^{-1} was measured for dibenzo[*b,h*]tetraphenylene.[10] The barrier to ring-inversion for tetraphenylene derivatives is commonly between 25 and 45 kcal mol^{-1},[11,12] thus, the central ring is essentially locked in place. In **3**, the twisting of the fluoranthene subunits should occur with a much lower barrier, either stepwise, among diastereomeric complexes, or correlated between enantiomers through an effective C_{2v} transition form.

The methyl groups of **3** appear as only a single set of signals in the proton NMR, expressing the time-averaged symmetry of the dynamically twisting racemate. If a frozen solution structure akin to that seen in the X-ray crystal structure could be obtained, two sets of methyl signals, *exo* and *endo*, should be seen. This would only be observable at lower temperatures.

In an attempt to measure the barrier to twisting in **3**, dynamic ^{1}H-NMR spectra were recorded at temperatures from -120 to 25 °C in dichlorofluoromethane-d.[13] However, no splitting of the signal set was observed, implying an upper limit to the twisting barrier of *ca.* 7.5 kcal mol^{-1}. This conclusion is given additional support by the recently reported barrier to twisting of 8,9-diacetoxy-1,6,7,10-tetramethylfluoranthene ($\Delta G^{\ddagger} < 7.0$ kcal mol^{-1}).[9]

Luminescence was observed during the isolation of **3**. This is not surprising given the fluorescent properties of the parent fluoranthene (**7**), however, perturbations of the electronic spectra of **3** could reveal something about the coupling between the juxtaposed chromophores. Thus, it was decided to study the photophysics of the series of fluoranthenes: 8,9-diphenyl-1,6,7,10-tetramethylfluoranthene (**9**),[14] and **3**.
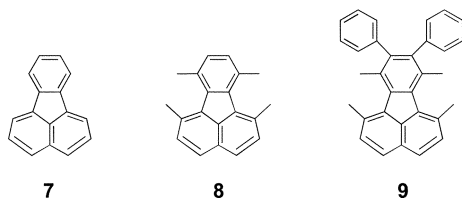
The UV λ_{max} displays a predictable red shift upon methyl or phenyl substitution (Table 1) concomitant with twisting of the plane. Somewhat surprising is the lack of any significant differences among **8**, **9**, and **3**, however, the severely distorted central ring prevents conjugation, and allows the two fluoranthene substructures to behave like isolated units. The only noticeable change is a slight increase in molar absorptivity. The change in the fluorescent emission throughout the series is one of spectral structure rather than wavelength. The parent displays two maxima, but only the longer wavelength emission persists in **8**, **9**, and **3**. The quantum efficiencies (ϕ_f) were measured by comparison to 9,10-diphenylanthracene in cyclohexane[15] and are the same, within experimental error. Thus, neither the severe

twisting of the methylated derivatives (**8** and **9**) nor the proximity of chromophores in **3** lead to any statistically relevant deviation in the quantum efficiency.

Notes and references

† CCDC reference number 255954. See http://www.rsc.org/suppdata/ob/b4/b416820h/ for crystallographic data in .cif format. Crystal data **3** ($0.30 \times 0.20 \times 0.10$ mm^3): Formula $C_{52}H_{40}$; formula weight 664.84; crystal system monoclinic; $a = 17.705(2)$ Å, $b = 21.289(2)$ Å, $c = 19.354(2)$ Å, $\beta = 96.336(3)^{\circ}$, $V = 7250.4(15)$ Å^3, $T = 296(2)$ K; space group $C2/c$; $Z = 8$; $m = 0.069$ mm^{-1}; $\rho = 1.218$ mg m^{-3}; reflections collected 18208; independent reflections 6303 [R(int) = 0.0306]; data/restraints/parameters 6303/0/477; goodness of fit on F^2 0.875; final R indices [$I > 2\sigma(I)$] $R1 = 0.0401$, $wR2 = 0.0997$; R indices (all data) $R1 = 0.0693$, $wR2 = 0.1080$; largest diff. peak and hole 0.126 and -0.134 e Å^{-3}.

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8 1,6,7,12,13,18,19,24-Octamethylacenaphthyleno[*b,l*]tetraphenylene (**3**). 6,7-Dihydro-6-hydroxy-7,9-dimethyl-8*H*-cyclopenta[*a*]acenaphthylene-8-one (**6**) (440 mg, 1.58 mmol) and 5,6,11,12-tetradehydrodibenzo[*a,e*]cyclooctene (**4**) (79 mg, 0.40 mmol) were dissolved in acetic anhydride (20 mL) under an argon atmosphere. The suspension was heated to 100 °C and gently stirred for 12 h. The resulting solution was cooled to ambient temperature, diluted with toluene (20 mL) and quenched slowly with 2 M NaOH. The organic layer was washed three times with additional 2 M NaOH (50 mL), dried over MgSO$_4$ and then passed through a short plug of silica gel. The crude product was purified by column chromatography on silica gel with 5% ethylacetate in hexane as the eluent to yield an orange solid (210 mg, 78%). Mp 354 °C (d). ^{1}H NMR (CDCl$_3$, 500 MHz), ppm: 2.47 (s, 12H), 2.70 (s, 12H), 7.21–7.26 (m, 8H), 7.29 (d, $^3J = 8$, 4H), 7.61 (d, $^3J = 8$, 4H) ^{13}C NMR (CDCl$_3$, 125 MHz), ppm: 22.5, 24.9, 126, 126.5, 126.53, 126.7, 129.7, 131.69, 131.72, 134, 135.1, 139.7, 141.6. UV (CH$_3$CN) l_{max}, nm (e): 250 (7 × 10^4), 277 (4 × 10^4), 288 (4 × 10^4), 298 (4 × 10^4), 338 (1 × 10^4), 373 (2 × 10^4). HRMS: found 664.3155, calcd. (C$_{52}$H$_{40}$) 664.3130.
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14 8,9-Diphenyl-1,6,7,10-tetramethylfluoranthene (**9**). 6,7-Dihydro-6-hydroxy-7,9-dimethyl-8*H*-cyclopenta[*a*]acenaphthylene-8-one (**6**) (552 mg, 2.0 mmol) and diphenylacetylene (373 mg, 2.1 mmol) were dissolved in acetic anhydride (20 mL) under an argon atmosphere. The suspension was heated to reflux and gently stirred for 3 d. The resulting solution was cooled to ambient temperature, diluted with toluene (20 mL) and quenched slowly with 2 M NaOH. The organic

Table 1 Photophysical properties of **3** and **7–9**

	λ_{max}/nm	λ_{em}/nm	ϕ_f
7	358	431, 455	0.20 ± 0.02
8	369	452	0.19 ± 0.02
9	374	458	0.21 ± 0.03
3	373	461	0.17 ± 0.02

layer was washed three times with additional 2 M NaOH (50 mL), dried over $MgSO_4$ and then passed through a short plug of silica gel. The crude product was purified by column chromatography on silica gel with 5% ethylacetate in hexane as the eluent to yield a yellow solid (371 mg, 45%). Mp 196–197 °C. ^{1}H NMR (CDCl$_3$, 500 MHz), ppm: 2.42 (s, 6H), 2.82 (s, 6H), 7.1–7.12 (m, 6H), 7.18 (d, ^3J = 7.5, 2H), 7.41 (d, ^3J = 8, 2H), 7.73 (d, ^3J = 8, 2H). ^{13}C NMR (CDCl$_3$, 125 MHz), ppm: 23.3, 24.7, 126, 126.2, 126.6, 127.5, 128.2, 130.8, 131.8, 132.1, 134, 135, 140, 141.6, 142.2. UV (CH$_3$CN) l_{max}, nm (e): 251 (7×10^4), 276 (3×10^4), 287 (4×10^4), 295 (3×10^4), 338 (1×10^4), 374 (1×10^4). HRMS: found 410.2024, calcd. (C$_{32}$H$_{26}$) 410.2029.

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