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Synthesis and structure of a twisted, colossal quinone

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Abstract

A very large quinone was prepared by the double Diels–Alder reaction of 2,5,9,12-tetra(*t*-butyl)diacenaphtho[1,2-*b*:1′,2′-*d*]thiophene and benzoquinone. The crystal structure of the polycyclic product shows that the central anthraquinone ring system is quite twisted (50°), and the overall structure possesses approximate D_2 symmetry. © 2000 Elsevier Science Ltd. All rights reserved.

The synthesis of fullerene fragments has been a fertile area of research. Most of the previous methods have used flash vacuum pyrolysis to overcome the inherent strain of the curved products but often suffer from poor yields.[1] However, recent successes with nonpyrolytic syntheses suggest that large-scale preparations of fullerene fragments may be possible if the appropriate precursors can be synthesized easily.[2–4] In an effort to prepare an assortment of large, nonplanar molecules, we have focused our efforts on targets which are assembled from substituted acenaphthene units.

2,5-Di(*t*-butyl)acenaphthene (**2**) was synthesized by Friedel–Crafts alkylation of acenaphthene with *tert*-butyl chloride and aluminum chloride in CS_2,[5] and this material was heated with sulfur to yield 2,5,9,12-tetra(*t*-butyl)diacenaphtho[1,2-*b*:1′,2′-*d*]thiophene (**3**) and the trimerization product **4** (Scheme 1).[6–8] Compound **4** has been prepared previously by direct alkylation of decacyclene with *tert*-butyl chloride.[9] Compound **3**[10] can be used as a building block for larger polycyclic products; similar thiophenes are known to be good dienes for Diels–Alder reactions.[11] In this light, **3** (200 mg, 0.36 mmol) was heated at reflux with 1,4-benzoquinone (19.43 mg, 0.17 mmol, 0.5 equiv.) in nitrobenzene (2.5 mL) for 40 hours. The reaction progress was monitored by TLC (silica gel, hexanes). Upon the disappearance of **3**, the reaction mixture was cooled, the crude product was precipitated with methanol (10 mL), and collected by filtration. The resulting solid was purified by TLC (silica gel, cyclohexane), and an orange fluorescent product, 2,5,8,12,15,18,21,25-octa(*t*-butyl)diacenaphtho[1,2-*l*:1′,2′-*l*′]benzo-[1,2-*j*:4,5-*j*′]difluoranthene-10,23-dione (**5**), was obtained in 5% yield (Scheme 2).[12]

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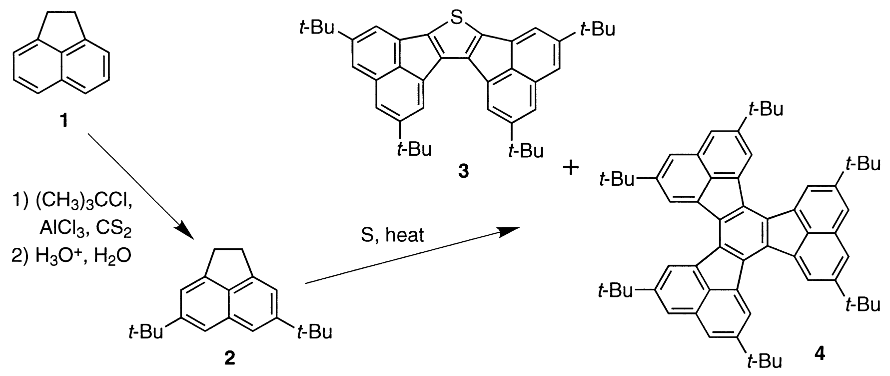
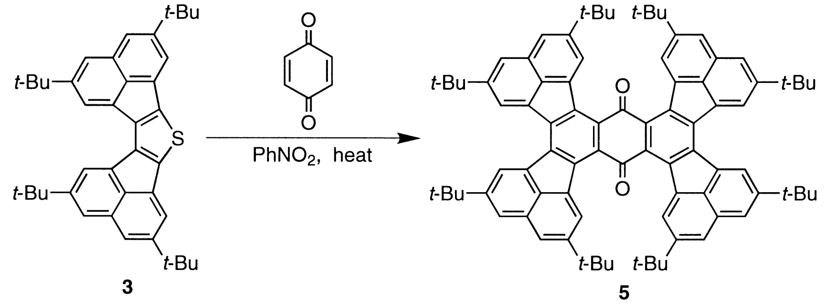


Scheme 1.



Scheme 2.

The geometry of **5** was initially examined by means of semiempirical MO calculations at the AM1 level.[13] A preliminary analysis revealed five possible conformations, one with C_i symmetry, two with C_2 symmetry, and two with D_2 symmetry (Table 1). The pairs of D_2 and C_2 structures differ in the orientation of the *tert*-butyl groups. After geometry optimization, the lowest energy conformation possessed C_2 symmetry. In this structure, the central quinone is a twist-boat with the C_2 axis perpendicular to the mean plane of the quinone. The overall C_2 structure is dome-shaped,

Table 1
Calculated energies (a.u.) of conformations of compound **5**. The relative energies (kcal/mol) of the conformations, normalized to the C_2 energy, are in parentheses, and the longitudinal twists of the anthraquinone in the D_2 conformations are in brackets

Symm.	AM1	HF/STO-3G	HF/3-21G
C_i	0.228101 (10.6)	−3416.100205 (10.2)	−3438.519511 (6.7)
D_2	0.226015 (9.3) [30.7°]		
	0.222586 (7.2) [29.9°]	−3416.109674 (4.2) [34.7°]	−3438.528143 (1.3) [30.3°]
C_2	0.212895 (1.1)		
	0.211148 (0.0)	−3416.116377 (0.0)	−3438.530236 (0.0)

which is an ideal conformation for the pursuit of curved fullerene fragments. In contrast to these calculations, however, a single crystal X-ray analysis of this material yielded a structure with approximate D_2 symmetry and an overall twist along the central anthraquinone moiety of 50.5° (see Fig. 1).[14] Interestingly, a search of the Cambridge Structural Database for anthraquinone derivatives containing nonhydrogen substituents on carbons 1–8 found only two structures; these possessed C_i and approximate C_{2v} symmetry.[17,18]

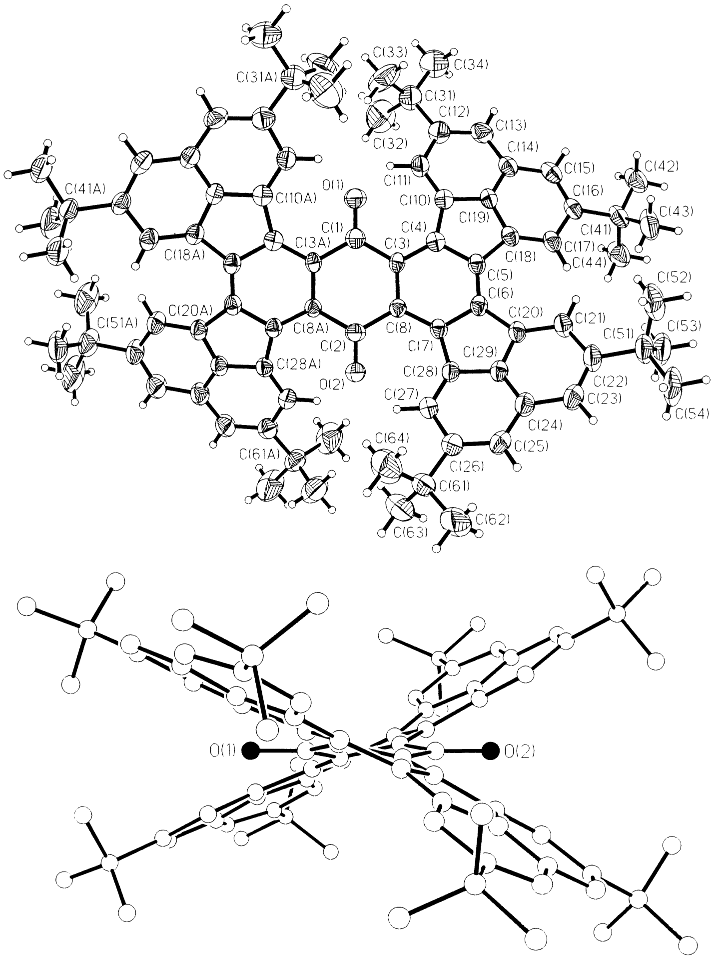


Figure 1. Two views of the molecular structure of quinone **5**. In the upper image, thermal ellipsoids have been drawn at the 50% probability level

Ab initio calculations at the HF/STO-3G and HF/3-21G levels[19] for the C_i conformation and the lower energy conformation of each of the C_2- and D_2-symmetric pairs revealed smaller differences between the various conformational minima. Most notably, the difference in energy between the C_2 and D_2 structures decreased to only 1.3 kcal/mol at the highest level employed. Given the observed trend in the calculated energies, it is conceivable that a calculation at a still higher level of theory might show the D_2 conformation to be the preferred geometry in the gas phase. The observed degree of twist is not reproduced in these calculations; all methods underestimated the twist by at least 15°. With such small differences in energy between the key conformations and a presumably soft potential energy surface, it is easy to imagine that the observed conformation and the relatively poor agreement of the experimental and observed twists may be due to crystal packing forces.

Quinone **5** is a molecule well-suited for further synthetic manipulation—in particular, the synthesis of fullerene fragments by the construction of additional fused rings by elaboration at the carbonyl groups. These and other reactions with compounds **3** and **5** are under investigation.

Acknowledgements

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10. Compound **3**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.53 (18H, s), 1.59 (18H, s), 7.74 (2H, s), 7.78 (2H, s), 7.85 (2H, s), 8.18 (2H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 31.86, 31.92, 35.71, 35.84, 118.84, 120.49, 121.67, 121.85, 128.90, 130.86, 132.85, 134.12, 151.60; HRMS: 556.3152; calcd for $C_{40}H_{44}S$ (M^+): 556.3164.
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12. Compound **5**: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.57 (36H, s), 1.67 (36H, s), 8.04 (4H, s), 8.06 (4H, s), 9.07 (4H, s), 9.60 (4H, s); ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 32.23, 36.05, 123.22, 124.18, 127.35, 129.71, 132.07, 135.14, 150.76, 152.29; FAB MS *m*/*z*: 1154 (M+H [$^{13}C_1$]).
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14. An orange prism of **5** (0.18×0.18×0.18 mm) was obtained by evaporation of a solution in ethyl acetate–acetone–ethanol. Crystal data: $C_{86}H_{88}O_2 \cdot 2C_4H_8O_2$; trigonal, space group $P3_221$; $a=b=16.5203$ (2) Å, $c=25.6779$ (4) Å, $V=6069.1$ (1) Å^3, $Z=3$, $D_{\text{calcd}}=1.091$ g/cm^3. Intensity measurements ($\theta \leq 45°$) were made on a Nonius KappaCCD diffractometer (Mo-Kα radiation, $T=200$ K). A total of 69,816 reflections were processed by using the programs DENZO and SCALEPACK[15] to give 5302 unique reflections ($R_{\text{int}}=0.094$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using Siemens SHELXTL.[16] All nonhydrogen atoms were refined anisotropically; hydrogens were included with a riding model. One of the *t*-butyl groups was disordered with an 8:2 ratio of components; light bond distance restraints were used for the minor component. The refinement converged to $R(F)=0.0516$, $wR(F^2)=0.1294$, and $S=1.046$ for 4272 reflections with $I>2\sigma(I)$, and $R(F)=0.0706$, $wR(F^2)=0.1424$, and $S=1.023$ for 5302 unique reflections, 482 parameters, and 3 restraints.
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