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Curious Reduction Products from a Strained Polycyclic Quinone

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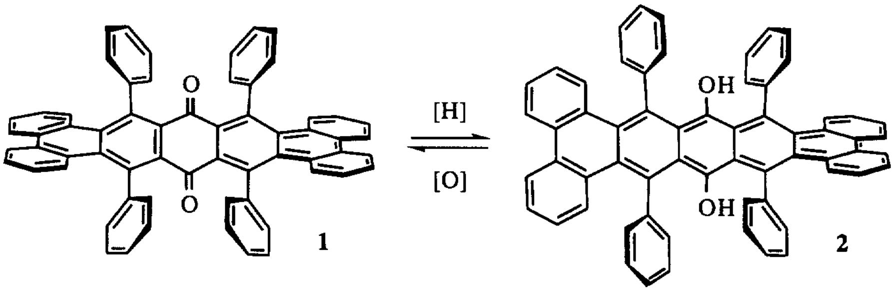
Abstract: Sodium borohydride reduction of 9,11,20,22-tetraphenyltetrabenzo[*a,c,l,n*]pentacene-10,21-dione (**1**), a strained polycyclic quinone, followed by an aqueous workup does not give the conventional hydroquinone **2**. Instead, reduction of an adjacent aromatic ring leads to the *cis*-9,22-dihydro compound **3** in which steric crowding is substantially relieved. © 1999 Elsevier Science Ltd. All rights reserved.

Many highly substituted acenes adopt twisted conformations with approximate C_2 or D_2 symmetry in the solid state.[1-4] The most extreme case is 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a,c*]naphthacene, where the end-to-end twist of the naphthacene core is 105°.[4] An interesting exception to this trend is the equally crowded 9,11,20,22-tetraphenyltetrabenzo[*a,c,l,n*]pentacene-10,21-dione (**1**), which instead adopts a C_i (and approximate C_{2h}) conformation in the solid state.[5] Although this molecule is distorted from planarity by nonbonded interactions between the phenyl groups and benzo hydrogens, it has no *overall* twist. AM1 calculations[6] are consistent with this observation and indicate that the C_{2h} conformation of **1** is preferred over a twisted D_2 conformation[7] by 9.0 kcal/mol (Table 1); interestingly, there also exists a bent C_2 conformation which is calculated to be 6.5 kcal/mol below C_{2h}-**1**, but it has not been observed. In contrast, a twisted C_2 conformation of the hydroquinone **2** is preferred by 4.5 kcal/mol over its C_{2h} conformation. The end-to-end twist for C_2-**2** is calculated to be an enormous 116°, so that a *very large, reversible conformational change* in the polycyclic aromatic framework of **1** and **2** might result from simple redox reactions.



1 **2**

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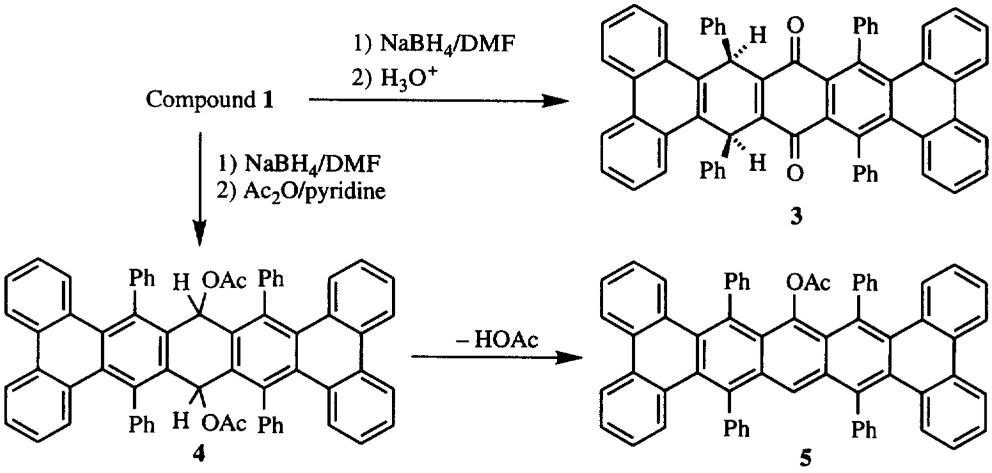
Table 1. Calculated Energies (AM1) of Polycyclic Quinones and Hydroquinones.

Compound	Conformation	ΔH_f (kcal/mol)	Imaginary Freq.	Exptl. Geom.
$C_{62}H_{36}O_2$				
Quinone **1**	C_2 (bent)	254.96	0	
	C_{2h}	261.42	0	C_i (~C_{2h})[5]
	D_2 (twisted)	270.40	3	
$C_{62}H_{38}O_2$				
Hydroquinone **2**	C_2 (twisted)	246.37	0	
	C_{2h}	250.83	0	
cis-9,22-Dihydro-**1** (**3**)	C_1	240.14	0	C_1
trans-9,22-Dihydro-**1**	C_2	243.42	0	
$C_{64}H_{40}O_2$				
Compound **5**	C_s	251.74	0	C_1 (~C_s)
	C_1 (twisted)	252.83	0	

Compound **1** is easily prepared,[5] but its reduction proved to be more difficult than expected. Treatment of **1** with several common reducing agents returned only unreacted starting material. The reductants included (a) Zn in refluxing 80% acetic acid, (b) aluminum isopropoxide or aluminum ethoxide in refluxing toluene, (c) hydrogen over 10% Pd on C in benzene, and (d) $TiCl_3$ in refluxing THF. Only hydride reagents such as $LiAlH_4$ and $NaBH_4$ gave partial or complete reduction. Cho and Harvey[8] have reported the reduction of a variety of polycyclic aromatic quinones with $NaBH_4$ in DMF, usually followed by treatment with acetic anhydride to trap the hydroquinones as their esters. These methods were employed for the reduction of **1**, but the isolated products were not the simple hydroquinones or their acetates!



Compound **1** was treated with an excess of $NaBH_4$ in DMF at 100 °C for 90 minutes. After cooling, acidification, and extraction, the bright orange reduction product **3** was isolated by preparative TLC (benzene) in 13% yield.[9] Yields of the reductions were invariably low due to the poor solubility of the quinone **1**; substantial unreacted **1** was always observed. The unusual structure of **3** (Figure 1) was established by X-ray analysis.[10]

Instead of the conventional hydroquinone, an adjacent aromatic ring has been reduced, and the two phenyl substituents on the ring adopt axial orientations at the prow and stern of the resulting "boat". It seems likely that the hydride reduction initially yields the hydroquinone **2**, but during the aqueous workup this tautomerizes to **3**. Tautomerization must occur after acidification; otherwise, the excess borohydride would further reduce the quinone. There is considerable driving force for this tautomerization; AM1 calculations indicate that the observed *cis*-dihydro compound **3** is 6.2 kcal/mol more stable than **2** as well as 3.3 kcal/mol more stable than its *trans* isomer, both due to the relief of steric conflicts between the benzo hydrogens and the phenyl groups.

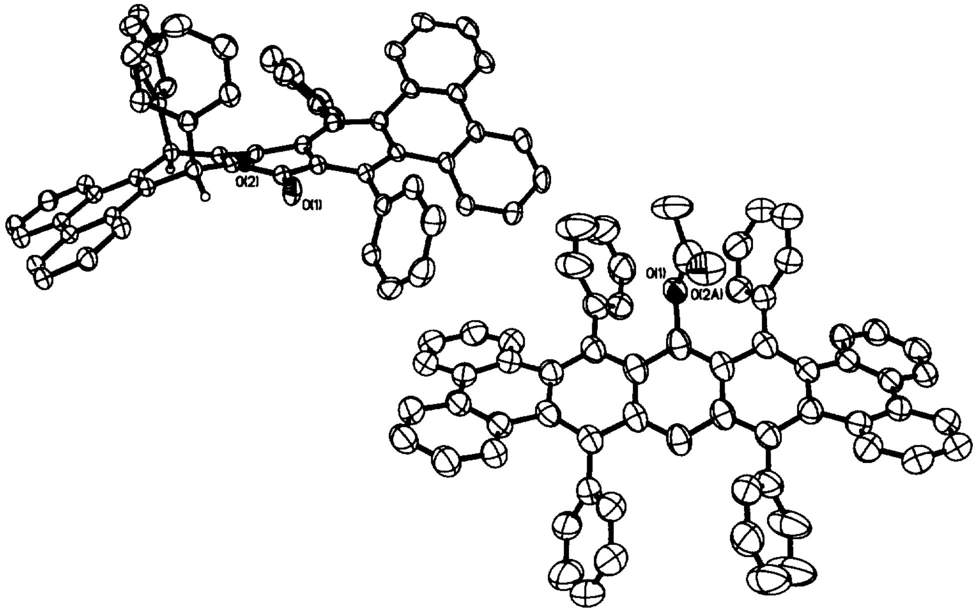


Figure 1. X-ray structures of compounds **3** (above) and **5** (below). Thermal ellipsoids have been drawn at the 50% probability level, and most hydrogen atoms have been omitted for clarity.

Although **2** is unstable with respect to **3**, it might be possible to capture the hydroquinone by acetylation *in situ*. Compound **1** was reduced as before, but prior to aqueous workup, acetic anhydride and pyridine were added and the mixture heated. Precipitation of the acetate(s) with water and fractionation of this material by preparative TLC once again yielded an orange solid, which appeared to be chiefly diacetate **4** (8% yield), which must result from two hydride reductions, not one. Its ^1H NMR spectrum was extremely complex, suggesting a mixture of isomers. Recrystallization of this material gave two types of crystals, the majority of which appeared by MS analysis to be **4**, but which were unsatisfactory for X-ray analysis [MS, *m/z* 900 (M^+, 46), 858 ($M - CH_2CO$, 25), 816 ($M - 2CH_2CO$, 100; exact mass 900.3244, calcd for $C_{66}H_{44}O_4$ 900.3239)]. However, a few bright orange crystals appeared by MS analysis to have lost acetic acid [MS, *m/z* 840 (M^+, 11), 812 ($M - CO$, 11), 798 ($M - CH_2CO$, 100)], and X-ray analysis showed this substance to be the aromatized monoacetate **5** (see Figure 1).[13] Compound **5** adopts a distorted conformation with no net twist very similar to that observed for **1** (see Figure 1); again, the observed structure is in accord with AM1 calculations (Table 1).

These experiments have yielded two very interesting polycylic aromatic structures, but they also suggest that the proposed redox-mediated conformational switching between the untwisted **1** and twisted **2** would not be indefinitely reversible, since the strained hydroquinone **2** can tautomerize to a more stable isomer such as **3** or, alternatively, undergo further reduction, as must have occurred in the formation of compounds **4** and **5**.

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References and Notes

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(7) A frequency calculation shows that D_2-**1** is not a even a potential minimum, but a three-dimensional transition state (see Table 1).

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(9) For **3**: ^{1}H NMR ($CDCl_3$) δ 6.56 (s, 2 H), 6.9-7.5 (m, 26 H), 7.56 (t, J = 8 Hz, 2 H), 7.66 (t, J = 9 Hz, 2 H), 8.21 (d, J = 9 Hz, 2 H), 8.37 (d, J = 9 Hz, 2 H), 8.78 (d, J = 9 Hz, 2 H); MS, *m/z* 814 (M^+, 33), 812 ($M - H_2$, 32), 798 (M – O, 66), 786 (M – CO, 100); exact mass 814.2857, calcd for $C_{62}H_{38}O_2$ 814.2872.

(10) Crystal data for **3**: $C_{62}H_{38}O_2{\bullet}3CH_2Cl_2$; triclinic, space group $P\bar{1}$; a = 11.5543(9) Å, b = 15.3293(12) Å, c = 16.8712(13) Å, α = 100.669(3), β = 106.344(3)°, γ = 109.432(2), V = 2572.6(3) Å^3, Z = 2, D_{calcd} = 1.381 g/cm^3. Intensity data were collected with $2\theta \leq 55°$ by using Mo Kα radiation (0.71073 Å) at 170 K on a Nonius KappaCCD diffractometer. A total of 29,438 reflections were indexed, integrated, and corrected for Lorentz and polarization effects (using the program DENZO[11]), and the data were scaled and merged to give 11,480 unique reflections (R_{int} = 0.085). The structure was solved by direct methods; nonhydrogen atoms were refined anisotropically, with hydrogens riding [C–H = 0.95, 0.99, or 1.00 Å, U(H) = 1.2U(C)] (SHELXTL[12]). The refinement converged to $R(F)$ = 0.0648, $wR(F^2)$ = 0.1698, and S = 1.143 for 8262 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.0907, $wR(F^2)$ = 0.1913, and S = 1.065 for 11,475 unique reflections, 705 parameters, and 3 restraints (5 reflections were suppressed).

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(13) Crystal data for **5**. $C_{64}H_{40}O_2$; monoclinic, space group $P2_1/c$; a = 10.1184(4) Å, b = 14.5100(6) Å, c = 14.8047(4) Å, β = 101.102(2)°, V = 2132.9(1) Å^3, Z = 2, D_{calcd} = 1.309 g/cm^3. Intensity data were collected and processed as described above for **3**: $2\theta \leq 45°$, 27,284 total reflections, 2792 unique reflections (R_{int} = 0.106). The molecule lies on a center of inversion but does not itself possess C_i symmetry, and the acetate moiety exhibits an additional two-fold disorder within the asymmetric unit. The net result is a four-fold disorder of the acetate across the inversion center, which was easily modeled. Nonhydrogen atoms were refined anisotropically, with hydrogens riding [C–H = 0.95 or 0.98 Å, U(H) = 1.2U(C), 1.5U(C_{methyl})]. Refinement converged to $R(F)$ = 0.0602, $wR(F^2)$ = 0.1352, and S = 1.163 for 1744 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.1116, $wR(F^2)$ = 0.1645, and S = 1.076 for 2792 unique reflections, 336 parameters, and 0 restraints.