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THE SOLID STATE STRUCTURE OF 9,11,20,22-TETRAPHENYLTETRABENZO[*a,c,l,n*]PENTACENE-10,21-DIONE: A LONGITUDINALLY TWISTED MOLECULAR RIBBON

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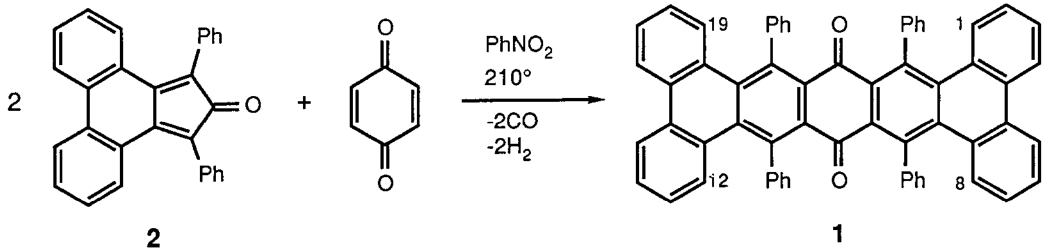
Summary: *An X-ray crystallographic analysis of the title compound (1) shows that this fused-ring polycyclic molecule is greatly distorted from planarity. The structure is centrosymmetric, and the mean plane of the center ring is twisted by approximately 48° relative to the plane determined by the terminal atoms of the pentacene nucleus.*

We recently reported the synthesis of 9,10-diphenyltetrabenz[*a,c,h,j*]anthracene, a polycyclic aromatic hydrocarbon with a 66° longitudinal twist.[1] We wished to prepare and characterize longer, more highly twisted polycyclic ribbons, and a review of the literature revealed a few previously described compounds which might exhibit such a structure. Foremost among these was 9,11,20,22-tetraphenyltetrabenzo[*a,c,l,n*]-pentacene-10,21-dione (1) first synthesized by Arbuzov *et al.* in 1939.[2]

We prepared compound **1** in one step by heating phencyclone[3] (**2**, 0.80 g, 2.09 mmol) and p-benzoquinone (0.108 g, 1.00 mmol) in refluxing nitrobenzene for 24 hours. Addition of methanol precipitated crude **1** (>90% pure) in 69% yield (0.56 g, 0.69 mmol). Small portions of this material were purified by silica gel column chromatography (solvent: toluene). Slow recrystallization of the product from toluene gave bright yellow prisms of **1** suitable for crystallography; mp >360° (lit.[2] 460-461°); ^{1}H NMR ($CDCl_3$) δ 7.02 (t, J = 8 Hz, 4H, 2,7,13,18-H_4), 7.3 (m, 20H, phenyls), 7.43 (t, J = 8 Hz, 4H, 3,6,14,17-H_4), 7.51 (d, J = 8 Hz, 4H, 1,8,12,19-H_4), 8.36 (d, J = 8 Hz, 4H, 4,5,15,16-H_4).



An X-ray crystallographic analysis[4] yielded the structure illustrated in Figure 1. Compound 1 resides on an inversion center in the crystal lattice, and, as expected, the polycyclic nucleus exhibits a nonplanar deformation. However, a single longitudinal twist is not observed; instead the pentacenedione is twisted in one direction and then equally in the reverse as required by the site symmetry. The two ends of the nucleus are coplanar, and the mean plane of the center quinone ring is twisted by 48.2° from these ends. The center ring exists in a chair conformation, while the remaining rings of the nucleus are shallow twist-boats. The nonplanar deformation must be due primarily to repulsion between the hydrogens attached to carbons 1, 8, 12, and 19 and the proximal carbons of the phenyl substituents. These nonbonded H-C distances are only 2.38 Å.

We are currently examining the possibility that reduction or other derivatization of this highly congested quinone will significantly alter its geometry, perhaps yielding a ribbon with a single large twist.

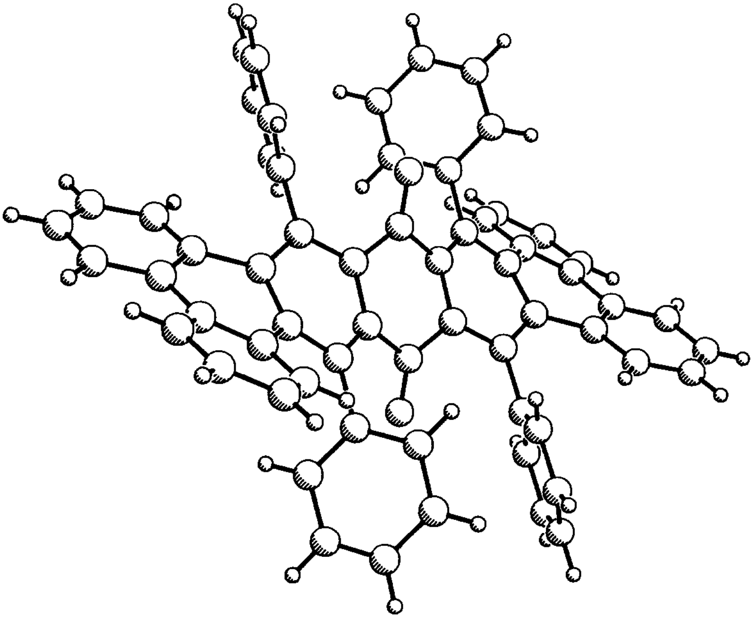


Figure 1. Computer-generated perspective drawing of compound 1.

REFERENCES AND NOTES

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2. Arbuzov, B.A., Abramov, V.S., and Devyatov, Ya.B. (1939) *J. Gen. Chem. USSR* **9**, 1559.
3. Dilthey, W., Henkels, S., and Schaefer, A. (1938) *Ber. Dtsch. Chem. Ges.* **71**, 974.
4. A crystal of compound **1** measuring 0.05 x 0.12 x 0.30 mm^3 was chosen for X-ray measurements. Crystal data: $C_{62}H_{36}O_2 \cdot 2C_7H_8$, FW = 997.3; monoclinic, space group $P2_1/n$; a = 11.242(3) Å, b = 12.598(6) Å, c = 19.228(5) Å, β = 98.56(2)°, V = 2692(1) Å^3, d_{calcd} = 1.23 g/cm^3. Intensity measurements were made with $3° < 2\theta < 114°$ using graphite monochromated CuKα radiation (λ = 1.54178 Å) at room temperature on a Nicolet R3m diffractometer. A total of 3623 reflections were measured, and after applying Lorentz, polarization, and decay corrections, 2681 were considered to be observed $[|F_0| > 3\sigma(F_0)]$. The structure was solved by direct methods using the SHELXTL software. The molecule is situated at the inversion center so that the assymmetric unit consists of half of the molecule **1** ($C_{31}H_{18}O$) plus a disordered toluene molecule. In the final cycles of blocked-cascade least-squares refinement, the nonhydrogen atoms of **1** were refined with anisotropic temperature factors, the toluene molecules (three positions were entered with occupancies of 0.50, 0.25, and 0.25) were refined as rigid phenyl groups with isotropic temperature factors, and all hydrogens were varied using a riding model. Final refinement with 333 parameters converged at R = 0.079 and R_w = 0.088 with goodness of fit = 1.45.

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