Twisted Polycyclic Aromatic Hydrocarbons. Structural Studies of Protic and Deuteriated 1,2,3,4-Tetraphenyltriphenylenes

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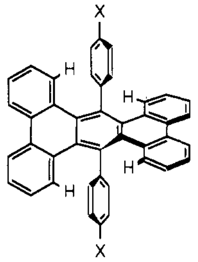
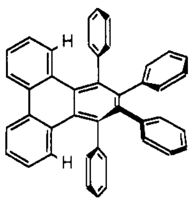
An X-ray crystallographic study of 1,2,3,4-tetraphenyltriphenylene shows that the polycyclic nucleus of this molecule is substantially twisted due to severe nonbonded interactions between the triphenylene hydrogen atoms and the proximal carbons of the 1- and 4-phenyl groups. The two independent molecules in the crystallographic unit cell exhibit twists of 28.1° and 30.9°, slightly less than the 33° twist predicted by MM2(85). 1,2,3,4-Tetraphenyl[5,6,7,8,9,10,11,12-$^2H_8$]triphenylene was prepared to determine if the twist angle would be altered by deuterium substitution, and it was found that the X-ray structures of the deuteriated and protic molecules did not differ significantly.

A variety of longitudinally twisted polycyclic aromatic hydrocarbons have recently been prepared and structurally characterized in our laboratory.[1] The most highly distorted of these are 9,18-diphenyltetrabenz[*a,c,h,j*]-anthracene and its derivatives (**1a–c**), which exhibit end-to-end twists of the anthracene nucleus ranging from 60.8° to 69.7° in the solid state,[1a,c] a result of nonbonded interactions between hydrogens on the benzo substituents and the proximal carbons of the phenyl groups (henceforth referred to as $H–C_{Ar}$ interactions). We wished to determine the type of distortion exhibited by the closely related hydrocarbon 1,2,3,4-tetraphenyltriphenylene (**2**), formally 4a,4b-*seco*-**1a**.



1a X = H
b X = Cl
c X = CF_3



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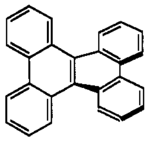

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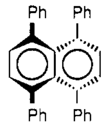

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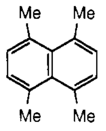

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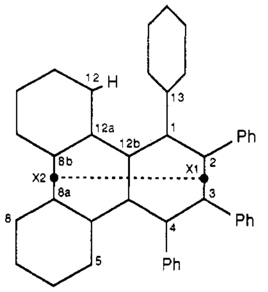
It was unclear to us whether compound **2** would respond to steric congestion by a twisting of the polycyclic nucleus as in **1** or instead by a bending of the phenyl substituents away from the benzo hydrogens with little or no distortion of the triphenylene nucleus. Both kinds of deformation might be observed, and in this regard we note that in the solid-state tetrabenzonaphthalene **3** exhibits an end-to-end twist of 34.9°,[2] 1,4,5,8-tetraphenylnaphthalene **4** is untwisted (but the rings of the naphthalene are distorted into shallow boat conformations),[3] and 1,4,5,8-tetramethylnaphthalene **5** is essentially planar (the peri contacts are reduced by "an in-plane splaying of ring–methyl bonds").[4]

A molecular mechanics calculation [MM2(85)[5]] yielded a structure for **2** with approximate C_2 symmetry, and it indicated that the triphenylene moiety would be twisted by 33.0°. (We define the nuclear twist as the dihedral angle 2–X1–X2–8b, where X1 and X2 are the centroids of carbons 2 and 3, and 8a and 8b, respectively.) The distance from the 12-H and phenyl carbon 13 (the $H–C_{Ar}$ contact) was estimated to be 2.41 Å, and little bending of the 1- and 4-phenyl groups away from the benzo hydrogens was predicted, as judged by the similarity of angles 12b–1–13 (121.7°) and 2–1–13 (118.2°) in the calculated structure.



A sample of compound **2** was prepared by the method of Dilthey et al.,[6] and single crystals were obtained easily from CH_2Cl_2–acetone. The space group is $P\bar{1}$, with $Z = 4$; the unit cell contains two *independent* molecules of **2**. The two molecules are illustrated in Figure 1 in their relative orientation in the lattice. In general, their geometries are quite close to the calculated structure. The nuclear twists of the two were 28.1° ± 0.4° and 30.9° ± 0.4°,[7] slightly less than predicted by MM2(85), and the four $H–C_{Ar}$ distances (two in each molecule) were correspondingly closer, averaging 2.34 ± 0.04 Å, but the angles of the types 12b–1–13 (121.3° ± 0.6°) and 2–1–13 (119.0° ± 0.7°) did not differ significantly from the calculated structure. Interestingly, when the steric energies of the two crystallographic structures of **2** were compared by using MM2(85),[8] a difference of only 0.3 kcal/mol was found.[9]

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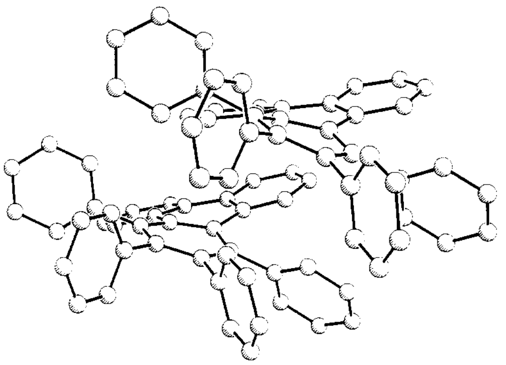


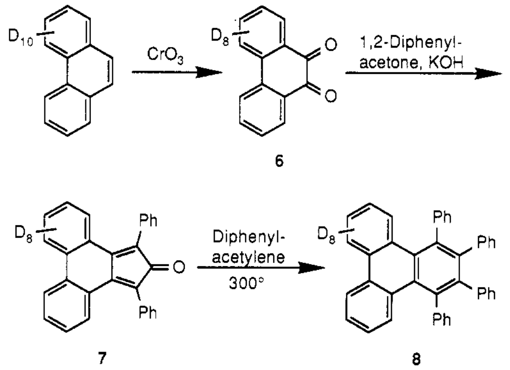
Figure 1. X-ray structures of the two crystallographically independent molecules of compound **2** illustrated in their relative orientation in the crystal. Hydrogen atoms have been omitted for clarity.

Table I. Crystallographic Data for Compounds 2 and 8

	2	**8**
formula	$C_{42}H_{28}$	$C_{42}H_{20}D_8$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	13.302 (3)	13.305 (4)
b, Å	14.882 (3)	14.869 (4)
c, Å	16.042 (4)	16.025 (4)
α, deg	75.39 (2)	75.50 (2)
β, deg	76.46 (2)	76.44 (2)
γ, deg	76.13 (2)	76.15 (2)
Z	4	4
V, Å^3	2932 (1)	2928 (1)
D_{calcd}, g cm^{-3}	1.21	1.23
crystal size, mm	0.05 × 0.10 × 0.42	0.36 × 0.50 × 0.51
μ, cm^{-1}	5.3 (Cu Kα)	0.6 (Mo Kα)
2θ range	3°–105°	3°–50°
reflectns measurd	$l > 0$	$l > 0$
unique reflectns	6739	10175
obsd reflectns[a]	4489	5569
parameters	757	757
least-squares refinmnt[b]	blocked cascade	blocked cascade
R (R_W)	0.062 (0.056)	0.081 (0.055)
goodness of fit	1.28	1.65

[a] Reflections were considered to be observed if $|F_o| > 3\sigma(F_o)$. [b] All carbon atoms were refined with anisotropic thermal parameters; hydrogen atoms were fixed at idealized positions (C–H = 0.96 Å, C–C–H = 120°) and refined isotropically.

The high distortion of the polycyclic nucleus due to the very short H–C_{Ar} distances in compound **2** is not terribly costly in energetic terms, however. MM2(85) calculations indicate that the steric energy of triphenylene itself (no phenyl substituents), which is planar, is only 4.2 kcal/mol lower than that of triphenylene constrained to be twisted by 33°. This finding suggested that small energetic differences might be reflected in detectable structural changes, and led us to wonder if deuterium substitution of the benzo hydrogens of **2** would lead to a change in geometry due to the smaller steric demands of deuterium. A multitude of deuterium kinetic steric isotope effects have been observed in isomerization reactions with highly crowded transition states,[10] and equilibrium steric isotope effects have been observed by NMR and circular dichroism,[11] but to our knowledge there have been no direct crystallographic comparisons of isotopomers of crowded organic molecules. The relative ease of synthesis and crystallization of compound **2** encouraged us to prepare it in deuteriated form to determine the structural effects, if any, of deuterium substitution at the critical benzo positions. 1,2,3,4-Tetraphenyl[5,6,7,8,9,10,11,12-$^2H_8$]triphenylene (**8**) was prepared from perdeuteriated phenanthrene as shown below, single crystals were obtained as before, and the structure was determined by X-ray analysis. No significant difference between the structures of the protic and deuterated molecules was found nor do we consider the small differences in the unit cell parameters (see Table I) to be significant. Even in this crowded molecule, the relief of steric strain afforded by deuterium substitution has no observable crystallographic manifestations at our present level of sensitivity.



Experimental Section

1,2,3,4-Tetraphenyltriphenylene (**2**) was prepared as described previously.[6] The slow evaporation of solutions of **2** in methylene chloride–acetone yielded single crystals suitable for X-ray analysis: mp >350 °C (lit.[6] mp 465 °C); ^{1}H NMR (CDCl$_3$) δ 6.68 (m, 4 H), 6.89 (m, 6 H), 7.01 (t, 2 H, J = 8 Hz), 7.07 (m, 10 H), 7.39 (t, 2 H, J = 8), 7.58 (d, 2 H, J = 8), 8.41 (d, 2 H, J = 8). [$^2H_{10}$]-Phenanthrene (98.7 atom % D) was obtained from Merck & Co.

[$^2H_8$]Phenanthrene-9,10-quinone (6). [$^2H_{10}$]Phenanthrene (1.00 g, 5.32 mmol) was dissolved in acetic acid (8 mL) at 60 °C. A solution of chromium trioxide (2.2 g, 22 mmol) in 5:2 acetic acid–water (7 mL) was added dropwise over 1.5 h. After a total of 2 h, the reaction mixture was poured into 1 M potassium carbonate (350 mL). This was shaken with toluene, and the organic layer was separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave orange crystalline [$^2H_8$]phenanthrene-9,10-quinone (0.968 g, 84% yield). This material was judged to be >95% pure by TLC (solvent, benzene; R_f 0.11), and it was used without further purification.

1,3-Diphenyl[4,5,6,7,8,9,10,11-$^2H_8$]cyclopenta[*l*]phenanthren-2-one (7). [$^2H_8$]Phenanthrene-9,10-quinone (0.70 g, 3.24 mmol) and 1,3-diphenylacetone (0.75 g, 3.57 mmol) were mixed in ethanol (15 mL). A solution of potassium hydroxide (0.2 g) in ethanol (1 mL) was added dropwise at room temperature. The quinone dissolved completely after about half of the base had been added. At this point the reaction mixture was immersed in a boiling water bath, and the remainder of the base was added. After heating 5 min, the reaction mixture was cooled in an ice bath for 15 min, and the black crystals of compound **7** were collected by filtration (0.627 g, 50% yield): mp 243–246 °C (lit.[6] mp [unlabeled] 273 °C); MS, m/z (relative intensity) 390 (M$^+$ [$^2H_8$], 100), 362 (M – CO, 93).

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(8) For these calculations, the crystallographic carbon coordinates were entered and fixed, while the hydrogen positions (which are less well determined by X-ray methods) were optimized by the program.

(9) It is important to note that the differences in the structures of the two crystallographically independent molecules of **2** must be due to crystal-packing forces. We previously observed a 9° variation in the twists of compounds **1a–c**;[1c] this variation might be due primarily to differences in crystal packing forces or, alternatively, to electronic substituent effects, but the relative contributions of the two cannot be estimated when only one structure of each molecule has been determined. While not resolving this issue, the fact that the nuclear twists of molecules of **2** do vary by 3° in the solid state shows that the crystal-packing forces can have a significant effect on the degree of molecular distortion in these already strained molecules.

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1,2,3,4-Tetraphenyl[5,6,7,8,9,10,11,12-$^2H_8$]triphenylene (8). The cyclopentadienone 7 (0.104 g, 0.267 mmol) and diphenylacetylene (0.3 g) were heated in a Pyrex screw-capped tube at 300 °C for 2 h. After cooling, the residue was taken up in methylene chloride. Methanol was added, and the product 8 crystallized after partial evaporation of this solution (51 mg, 35% yield). One recrystallization of this material from methylene chloride–acetone gave crystals suitable for X-ray analysis: mp >350 °C (lit.[6] mp [unlabeled] 465°); ^1H NMR ($CDCl_3$) δ 6.68 (m, 4 H), 6.89 (m, 6 H), 7.07 (m, 10 H); MS, m/z (relative intensity) 540 (M^+ [$^2H_8$], 100), 463 ($M - C_6H_5$, 15), 384 ($M - 2C_6H_6$, 10). Isotope ratio analysis indicated that 87% of the molecules contained 8 deuteriums, 10% contained 7, 2% contained 6, and <1% contained 5 or fewer.

X-ray Crystallography. Crystallographic measurements were made on a Nicolet R3m diffractometer at 295 K. Graphite monochromated Cu Kα radiation (λ = 1.54178 Å) was used for crystallographic measurements on 2, and Mo Kα radiation (λ = 0.71069 Å) was used for the measurements on 8. The crystallographic data and details of data collection are reported in Table I. The supplementary material contains more detailed descriptions of the data collection and processing, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds 2 and 8.

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Registry No. 2, 36262-81-4; 6, 113451-49-3; 7, 113474-60-5; 8, 113451-50-6; [$^2H_{10}$]phenanthrene, 1517-22-2; 1,3-diphenylacetone, 102-04-5; diphenylacetylene, 501-65-5.

Supplementary Material Available: Crystallographic data collection and processing descriptions, final atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds 2 and 8 (20 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Archetypical Donor–Acceptor–Donor (D_2A) Molecules

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The primary objective of the present investigation was to study a class of compounds in which two donors and one acceptor (D_2A) are parts of the same molecule: **3a–e**. Systematic variation of the donor moiety ($ArCH_2$; Ar = C_6H_5, p-$MeOC_6H_4$, p-$NO_2C_6H_4$, β-naphthyl, p-$NH_2C_6H_4$ (**3a–e**)) leads to a series of compounds that behave in solution to a large extent like substituted TCNQ molecules. In contrast, the isomorphous mode of aggregation in the solid state for **3a**, **3b**, and **3d** indicates a strong driving force toward segregated stacking of the TCNQ moieties, a packing arrangement not observed in other TCNQ derivatives. The solid-state spectral properties also indicate the crucial role of the mode of aggregation. The relevance of these compounds to an overall strategy of design of organic conducting materials is discussed.

Introduction

To obtain conducting electron donor–acceptor (EDA) complexes, several minimal necessary requirements must be met simultaneously.[1–8] Strategies for achieving most of those requirements are known. But ultimately the overall problem is one of multiparameter optimization which is not easily realized, unless by default or serendipity. We have recently proposed[3b] that the molecular unit D_mA_n, 1, in which m donors are linked to n acceptors, possesses sufficient flexibility to optimize simultaneously a few, if not all, of the requirements. The most acute requirement is the architectural problem, namely, the aggregation in the solid state of both donors (D) and acceptors (A) in segregated stacks. Most of the known EDA complexes aggregate in mixed stacks (...DADA...) which are at best semiconductors.[9] Our rationale has been[3b] that for properly designed molecules, of the type 1, the sheer propensity for close packing may exert enough driving force to generate segregated-stack solids. Thus for example a D_2A molecule would have a tendency to produce the solid 2 if this rationale is indeed correct.

$D_m{-}{-}{-}A_n$

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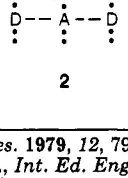

2

In addition, the molecule D_mA_n possesses a potential ρ value which may be fixed by the stoichiometric ratio m/n. Thus, for sufficiently powerful donor and acceptor molecules, n electrons will flow from D_m to A_n to provide an ionic ground state with $\rho_D = n/m$ and $\rho_A = 1$ (if $n < m$).

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