Helical Structures

Rational Design of Helical Columnar Packing in Single Crystals**

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Helices and superhelices are ubiquitous in nature and are key structural features of proteins, nucleic acids, and oligosaccharides. Therefore, chemists have made significant efforts to introduce helicity into artificial systems.[1] The most widely used strategy for generating supramolecular helices requires a nonconvalent motif which can provide the desired connectivity of the building blocks in a predictable manner. In this regard, hydrogen bonds,[2] metal–ligand coordination,[3] and π,π interactions[4] are often utilized.

We are actively involved in the design of molecular crystals and liquid-crystalline materials based on the self-assembly of polycyclic aromatic hydrocarbons (PAHs).[5] While there are many reports of the inclusion of chiral centers in discotic molecules inducing a regular helical bias,[4c,6] it is otherwise relatively rare to experimentally observe a helical columnar arrangement.[7] This is an attractive target for organic electronic materials, since such a helical columnar arrangement leads to exceptional one-dimensional

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Supporting information for this article (full details of the calculations, equilibrium structures, and Mulliken charge distributions of compounds **1** and **2** as well as ESP charge distributions for compound **1**) is available on the WWW under http://www.angewandte.org or from the author.

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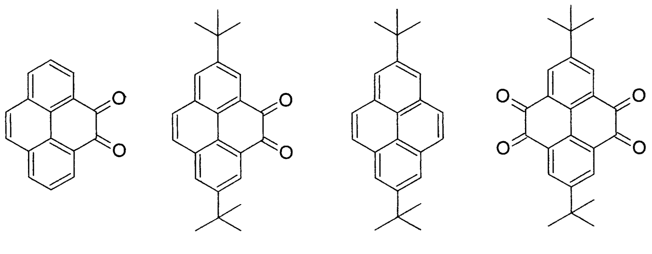
charge-carrier mobilities along the columns.[8] Herein we report the remarkable highly ordered, helical columnar packing of pyrene-4,5-dione derivatives in single crystals. This study represents a first step towards the rational design of crystalline helical columnar arrangements.

Recently, a weak dipole–dipole interaction has been utilized for inducing a columnar phase.[9] We planned to use a simple and nonchiral aromatic system to generate a helical superstructure in a crystalline state with weak interactions. We chose pyrene-4,5-dione derivatives (Scheme 1) as model compounds as the CO-CO moiety would generate a dipole which would be expected to organize the molecules in an antiparallel manner to produce a columnar structure. Furthermore, the introduction of bulky *tert*-butyl groups could modify the helical columnar arrangement, the self-assembly of which is controlled by a combination of dipole–dipole interactions and steric factors.


1 **2** **3** **4**

Scheme 1. Chemical structure of the model molecules.

Pyrene-4,5-dione has been used extensively to study the corresponding K-region oxide.[10] In addition, pyrene-4,5-dione participates in a variety of useful cyclization reactions.[11] It is thus surprising that little effort has been devoted to solving the crystal structures of its simple derivatives.[12] We find that the crystal of pyrene-4,5-dione (**1**)[10b] is arranged in an alternating stacked array (Figure 1 a) and not the sandwich herringbone packing exhibited by pyrene.[13] Unlike nitrated triphenylenes that have a tilt angle of approximately 41°,[9c] the stacked columns are tilted at an angle of only approximately 11° to the "best plane" through the aromatic core. The average perpendicular separation between the discs is 3.54 Å, which is close to the distance between dimers found in crystal structures of pyrene.

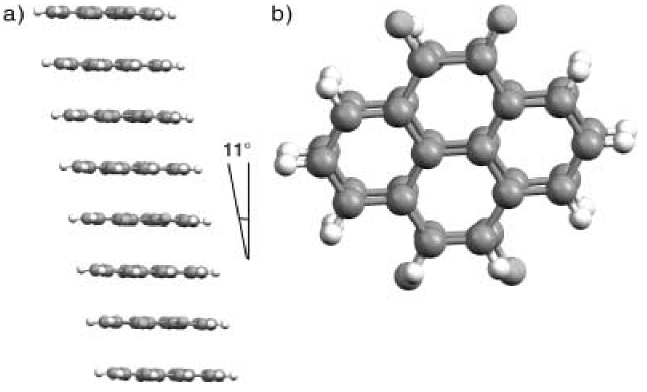


Figure 1. Stacking of pyrene-4,5-dione (**1**): a) arrangement along a columnar stack; b) view of two neighboring molecules projected onto the molecular planes showing the displacement of the molecules in the stacks.

Figure 1 b shows a pair of pyrene-4,5-dione molecules that give the visual impression of a super disk, that is, a dimeric species in which two rings of the near-planar portion of one molecule effectively overlap with the corresponding rings of the neighbor. Such an efficient overlap is highly unusual since most of the smaller PAHs crystallize in a fashion such that there is maximal packing density with only a small π,π interaction.[14]

According to quantum chemical calculations,[15] **1** has a large dipole moment (6.1–6.7 D). The maximum dipole–dipole stabilization would correspond to a configuration in which cofacial molecules are not offset. However, this molecular arrangement would lead to high π-electron repulsions.[16] Thus, the slightly offset geometry observed here with a tilt angle of 11° can be rationalized as being the best balance between the attractive dipole–dipole interaction and the π-electron repulsions. The dipole–dipole interaction between the pair of pyrene-4,5-dione molecules is estimated to be around 9.8–11.6 kcal mol^{-1}.[15]

A further step towards the control of supramolecular helical species concerns the number of residues per turn and the pitch of the helix, as well as the generation of the real three-dimensional, organized helical columnar arrangement by self-assembly. Inclusion of 2,7-di-*tert*-butylpyrene-4,5-dione (**2**),[17] 2,7-di-*tert*-butylpyrene (**3**),[18] and 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (**4**)[18] will be revealing since the face-to-face overlap of two neighboring rings is now unfavorable. It is expected that the combination of the dipole–dipole interaction and steric crowding should modify the helical arrangement of this simple model system.

A common feature in the packing behavior of **3** (Figure 2) and **4** (Figure 3) is the segregation of regions that contain the *tert*-butyl groups and the aromatic cores. In both cases, lamellar structures result from this microphase separation. Another common feature is that no significant interactions are observed between the aromatic cores. It is quite clear that **3** and **4** cannot form close cofacial packing without the driving force of dipole–dipole interactions.

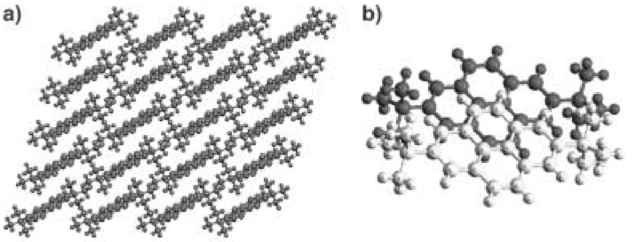


Figure 2. Packing pattern of 2,7-di-*tert*-butylpyrene (**3**): a) crystal structure of **3** viewed along the *b* axis; b) view of two neighboring molecules projected onto the molecular planes showing the displacement of the molecules in the stacks.

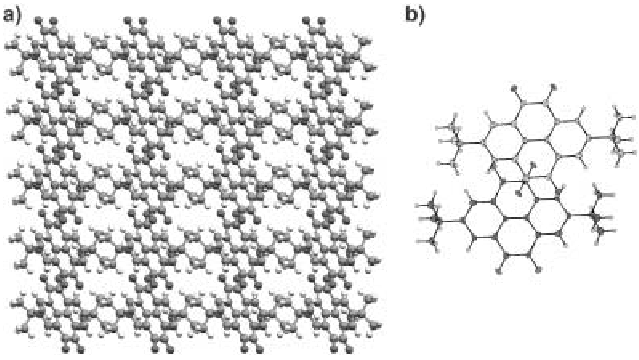


Figure 3. Packing pattern of 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (**4**): a) crystal structure of **4** viewed along the *b* axis; b) view of two neighboring molecules projected onto the molecular planes showing the displacement of the molecules in the stacks.

The enforced helical arrangement of compound **2** was confirmed by single-crystal X-ray analysis. The molecules are not strictly planar, but slightly bent; the largest deviation from the plane is the C–O bond (up to 0.3 Å). Interestingly, the crystal structure of **2** exhibits a modified three-dimensional, highly organized, helical columnar packing as well as the common feature of close cofacial packing of polar subunits. The asymmetric unit cell contains three independent molecules of **2** and one additional CH_2Cl_2 solvent molecule. The successive disks are rotated relative to each other by a "threefold" rotation of approximately 120° to accommodate the *tert*-butyl groups and obtain an efficient columnar packing (Figure 4a). Thus, the packing of **2** in the crystal can be described as a helical structure with three disks per turn and a pitch of 10.77 Å. The circular-shaped columns are arranged on a nearly square lattice with dimensions of 24.65 and 22.35 Å. The small deviation is probably a consequence of the molecular shape (Figure 4b). The solvent molecules are located between the columns in the interstitial volume, that is, they are included to fill the voids and take no active part in the interstack interactions.

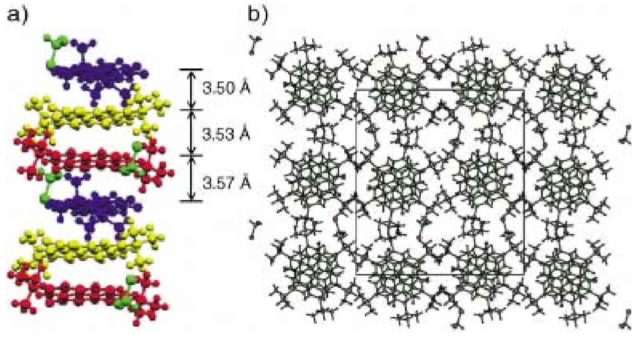


Figure 4. Stacking of 2,7-di-*tert*-butylpyrene-4,5-dione (**2**): a) arrangement along a columnar stack; b) view of the helical columns perpendicular to the plane of the molecules.

It should be noted that the tendency of **2** to build up a helical structure is independent of the solvent used in the crystallization. Isomorphous crystals of the same composition and with virtually identical lattice parameters and coordinates were obtained from ethanol ($(\mathbf{2})_3\cdot$EtOH).[12] The observation that identical structures are formed from different solvents is strong evidence that the helical columnar packing is an intrinsic property of **2**.

The interplanar distances of 3.50–3.57 Å observed in the crystal structure of **2** (Figure 4a) are also almost equal to that found in pyrene and pyrene-4,5-dione (**1**). Figure 5 shows three neighboring molecules projected onto the molecular planes; this arrangement suggests that the dipole–dipole interaction must be significant not only between two nearest neighbor molecules but also between two second nearest neighbor molecules. The role of dipole–dipole interactions in determining the reciprocal orientation of two nearest neighbor and two second nearest neighbor molecules is particularly evident. Indeed, although steric hindrance prevents the best reciprocal antiparallel orientation, dipole–dipole interactions drive the reciprocal orientation close to 120°, which still ensures a large attractive contribution. The dipole–dipole interaction between two nearest neighbors is estimated to be around 5.5–6.1 kcal mol^{-1}.[15] This packing preference can thus be attributed to a combination effect of maximized dipole–dipole interactions and the compatible accommodation of bulky *tert*-butyl groups.

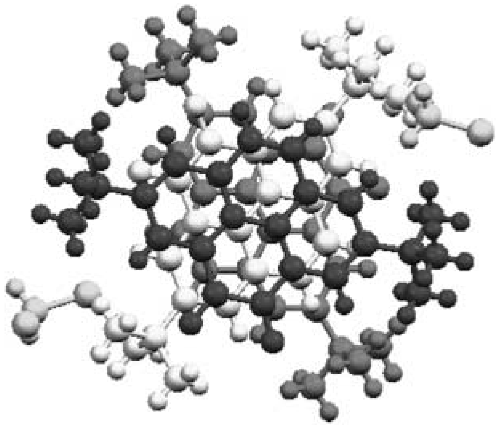


Figure 5. View of three neighboring molecules projected onto the molecular planes showing the displacement of the molecules in the stacks.

We have illustrated a rational approach towards helical superstructures with predictable three-dimensional organization in the crystalline state. While other strategies for encoding helicity in self-assembled columnar arrangements have been reported,[6a,9c] this approach offers advanced control of the overall superstructure. Further investigations are necessary to assess whether our approach can be generalized to control the self-assembly of molecules with aromatic cores. In addition, the CO-CO moiety provides active sites for further coordination, for example, towards potential application as molecular magnetic materials. This strong tendency to form self-assembled, well-defined helical columns also makes the title molecules promising candidates for liquid-crystalline materials. We are currently investigating this by introducing long alkyl chains.

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[12] The Cambridge Structural Database (CSD) contains no structures of pyrene-4,5-dione derivatives. Crystals of pyrene-4,5-dione (**1**), 2,7-di-*tert*-butylpyrene-4,5-dione (**2**', 2,7-di-*tert*-butylpyrene (**3**), 2,7-di-*tert*-butylpyrene-4,5,9,10-tetranone (**4**) suitable for X-ray structure analysis were obtained by slow evaporation of their dichloromethane or ethanol solutions at room temperature. Although the crystal structure of **3** has been previously reported (A. C. Hazell, J. G. Lomborg, *Acta Crystallogr. Sect. B* **1972**, *28*, 1059–1064), there is no detailed information about its packing behavior. Data collections for the crystal-structure analyses were performed on a Nonius KCCD diffractometer with graphite monochromated MoK_α radiation. The temperature was 120 K. The structures were solved by direct methods (Shelxs) and refined on F with anisotropic temperature factors for all non-hydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode. **1**: $C_{20}H_{16}O_2$, monoclinic, space group $P2_1/n$, $a=7.2913(4)$, $b=9.0849(5)$, $c=15.5725(7)$ Å, $\beta=96.919(1)°$, $V=1024.0(1)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.506\ \text{g cm}^{-3}$, unique reflections measured 2821, 790 reflections observed ($I>3\sigma(I)$), $R=0.0446$, $R_w=0.0486$. **2**: $(C_{24}H_{24}O_2)_3{\cdot}CH_2Cl_2$, monoclinic, space group $P2_1/c$, $a=10.7680(5)$, $b=24.6505(8)$, $c=22.3453(8)$ Å, $\beta=92.601(1)°$, $V=5925.1(4)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.254\ \text{g cm}^{-3}$, unique reflections measured 13243, 2979 reflections observed ($I>3\sigma(I)$), $R=0.0491$, $R_w=0.0283$; $(C_{24}H_{24}O_2)_3{\cdot}C_2H_5OH$ monoclinic, space group $P2_1/c$, $a=10.7593(6)$, $b=24.7864(8)$, $c=22.2712(8)$ Å, $\beta=92.185(1)°$, $V=5935.1(7)$ Å^3, $Z=4$, $\rho_{\text{calcd}}=1.208\ \text{g cm}^{-3}$, unique reflections measured 9838, 3714 reflections observed ($I>3\sigma(I)$), $R=0.0824$, $R_w=0.0912$. **4**: $C_{12}H_{11}O_2$, triclinic, space group $P\bar{1}$, $a=6.3273(4)$, $b=9.0975(6)$, $c=9.2448(6)$ Å, $\alpha=64.874(1)$, $\beta=96.919(1)$, $\gamma=72.543(1)°$, $V=459.5(2)$ Å^3, $Z=2$, $\rho_{\text{calcd}}=1.353\ \text{g cm}^{-3}$, unique reflections measured 2380, 713 reflections observed ($I>3\sigma(I)$), $R=0.0622$, $R_w=0.0653$. CCDC-223167 (**1**), CCDC-223168 (**2**), CCDC-223169 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] The dipole moments of **1** and **2** were obtained at HF/6-31G* and BLYP/6-31G* levels of theory using molecular structures optimized at the same level. The magnitude of the dipole–dipole interaction was estimated by employing the following equation: $E_{\mu,\mu'}=\frac{\mu,\mu'}{r^3}(2\cos\vartheta\cos\vartheta'+\sin\vartheta\sin\vartheta'\cos\xi)$ where r is the distance between the mass centers of the two molecules, θ and θ' are the angles formed by the dipole vectors with the r axis, and ξ is the dihedral angle formed by the two dipole vectors. Full details of the calculations, equilibrium structures, and charge distributions are included in Supporting Information.

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