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π-Complexation in the Solid State Induced by Intermolecular Hydrogen Bonding[†]

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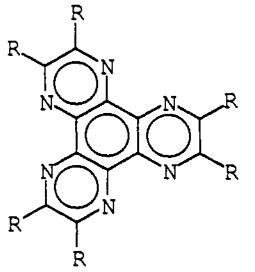
Abstract: Electron-deficient heterocycles, such as the hexaazatriphenylenes, avoid π-complexation in the solid state. We observe that interplane amide hydrogen bonding controls secondary structure and induces π-complexation in the solid state of an organic hexaamide predisposed to avoid it.

Because many of the useful macroscopic properties of materials are engendered by molecular organization, the control of solid-state assembly is of current interest. For example, second-order nonlinear optical response by a crystal requires noncentrosymmetry;[1] engineering the necessary solid-state ordering may be approached in intellectually satisfying ways.[2] Bulk conductivity is likewise related to solid-state structure. Conducting organic solids often display Coulombically unfavorable cationic π-stacks.[3] It is likely that the conductivity of organic polymers is limited in part by poor interstrand association, since association would provide a pathway past chain defects.[4] We have considered whether intermolecular hydrogen bonding might be used to engender π-overlap in an organic material predisposed to avoid it. Of course, multiple amide–amide hydrogen bonds are employed by nature for control of secondary structure in proteins;[5] the molecular packing of even simple amides generally displays interlinked H-bonded rings forming ribbons with their axes arranged in parallel planes.[6] We now report that the occurrence of multiple amide hydrogen bonding induces the formation of stacked, π-complexed dimers in the solid state of an organic hexaamide.



1, R = CN
2, R = CONH$_2$
3, R = CO$_2$H
4, R = CO$_2$CH$_3$
5, R = CON(CH$_3$)$_2$

Hexaazatriphenylene (HAT) derivatives **1-5**[7] are strongly electron-deficient heterocycles, as demonstrated by: (1) their high reactivity toward base, (2) the fact that the cyclic voltammogram of hexanitrile **1** in acetonitrile reveals *four* reversible one-electron reductions,[8] and (3) the observation that compounds **1–4** form colored charge-transfer complexes with various π-bases (e.g., indole) with no observable propensity to form complexes with π-acids. Thus, it appeared likely that the heterocycle would be predisposed to avoid self-π-complexation; X-ray analyses of many other electron-deficient aromatic heterocycles support this view, as documented in Table 1.[9–18] However, hexaamide **2** appeared uniquely capable of associating *via* intermolecular multiple hydrogen bonding; indeed, the solubility of **2** is extremely limited as compared to those of **1**, **3**, **4**, and even **5**, which has H-bond acceptor but not donor sites. The crystallization of **2** was accomplished using slow water vapor diffusion into DMSO solution, **3** was crystallized from water containing 1,2,3,4-BTA, and **4** was crystallized from CH$_3$CN/MeOH (9:1).[19] Hexaamide **2** yielded two crystal types, trigonal (form A) and triclinic (form B); the only known difference in crystal growth procedures was that form B grew in a system disturbed for examination at irregular intervals, whereas form A grew in a system undisturbed for several months. The X-ray structures of **3** and **4** reveal rigorous avoidance of HAT–HAT π-stacking;[20] this trend is observed likewise in the

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[†] This paper is dedicated to the memory of Margaret C. Etter.

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(8) $E°$ (V vs SCE) values in acetonitrile are –0.01 (0/1–), –0.36 (1–/2–), –1.13 (2–/3–), –1.88 (3–/4–). The peak for the (1–/2–) couple is split, showing also at –0.53 V; the splitting is attributed to dimerization of the anion, which is not observed in DMF. $E°$ (V vs SCE) values in DMF are –0.02 (0/1–), –0.37 (1–/2–), –1.01 (2–/3–); the (3–/4–) couple is beyond the DMF solvent limit.

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(19) The 1,2,3,4-BTA (butanetetracarboxylic acid) was included in an effort to afford cocrystallization; crystals obtained did not include 1,2,3,4-BTA. Space groups, unit cell parameters, and *R*-factors for these samples follow: **2** (form A), trigonal, $P321$, $a = b = 13.558(2)$ Å, $c = 11.108(2)$ Å, $R = 0.242$ (most probably due to an inability to model all of the randomly disordered solvent, since potential alternative space group choices have been extensively investigated); **2** (form B), triclinic, $P\bar{1}$, $a = 12.723(4)$ Å, $b = 13.430(2)$ Å, $c = 8.737(7)$ Å, $\alpha = 103.54(3)°$, $\beta = 99.02(5)°$, $\gamma = 92.72(4)°$, $R = 0.055$; **3**, monoclinic $C2/c$, $a = 12.204(5)$ Å, $b = 25.337(3)$ Å, $c = 8.077(3)$ Å, $\beta = 102.54(3)°$, $R = 0.067$; **4**, monoclinic, $P2_1/n$, $a = 8.038(2)$ Å, $b = 27.284(2)$ Å, $c = 12.164(2)$ Å, $\beta = 106.42(2)$, $R = 0.057$.

(20) Pertinent portions of the structures of compounds **3** and **4** are provided as supplementary material. In **3**, the hydrogen bonding is to water oxygen acceptors.

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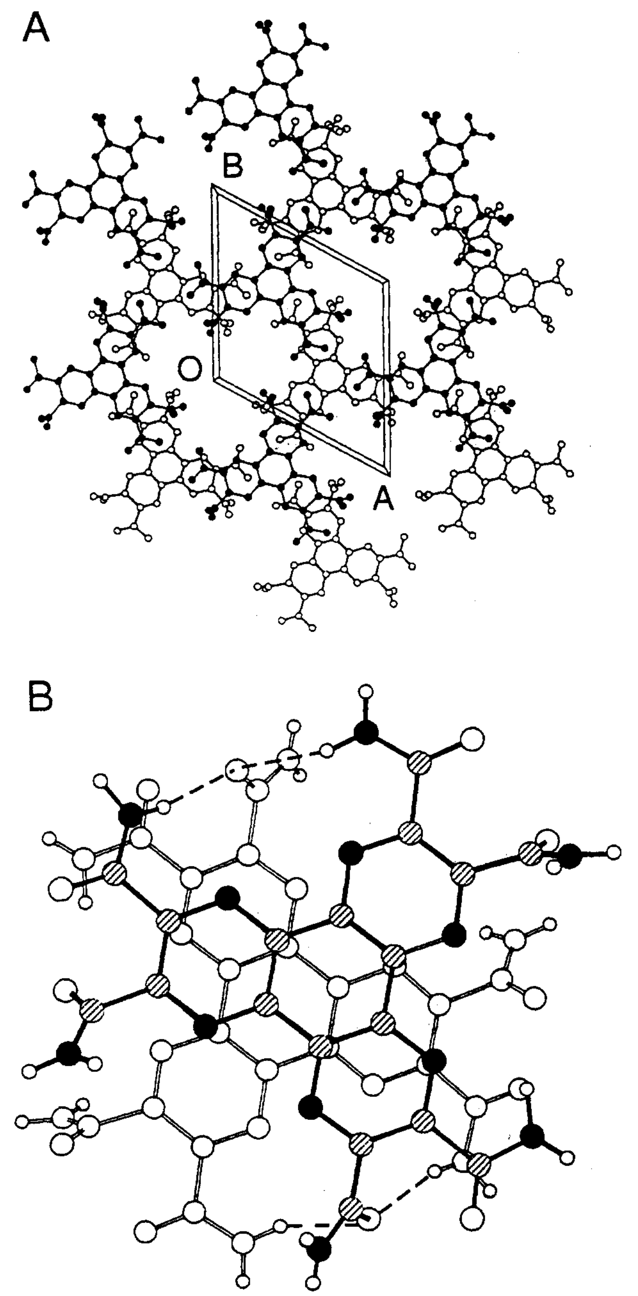

Figure 1.

Table 1. Summary of Cofaciality and Interplanar Distances for Crystalline Structures of Several Electron-Deficient Heterocycles[a]

substance	cofaciality	interplanar distance(s), Å	ref
o-phenanthroline	no		9
1,3-diazanaphthalene	yes	3.48, 3.53, 3.62, 3.46	10
2,3-diazanaphthalene	yes	3.53	11
1,8-naphthyridine	no		12
1,5-diazanaphthalene	yes	3.56, 3.82	13
2,6-diazanaphthalene	no		13
2,7-diazanaphthalene	no		14
9,10-diazaphenanthrene	yes	3.49	15
α-phenazine	yes	3.49	16
acridine, form II	yes	3.49, 3.61	17
acridine, form III	yes	3.47	18

[a] An interplanar distance of ~3.5 Å corresponds to the sum of van der Waals radii; a distance of ~3.3 Å is consistent with significant π-complex formation.

provisional structure of the trigonal form of **2** (Figure 1, form A).[21] In each of these structures, molecules in adjacent layers were offset significantly with respect to one another; further, the interlayer spacings in **3** and **4** [3.86(9) and 3.87(5) Å, respectively] were found to be larger than the expected van der Waals sum of 3.54 Å.[22]

However, the triclinic form of hexaamide **2** reveals intra- and intermolecular hydrogen bonding with concomitant stacking and heterocyclic π-complexation. The hexaamide molecules stack in a closely packed arrangement, although the spacing of the molecules in the stack is not uniform. Rather, closely spaced dimers are observed with a one-half ring offset that permits HOMO–LUMO overlap (Figure 1, form B). Dominating the dimer structure are two bifurcated interplanar H-bonds,[23] indicated by dashed lines in Figure 1, that serve as noncovalent "clamps" holding the dimer together; such 3-D amide–amide H-bonding is reminiscent of the α-helical motif observed in many polypeptides. *The mean interplanar distance of the HAT rings within these dimers, 3.32(10) Å, is smaller than the sum of van der Waals radii and consistent with π-complexation.*[24] This interplanar distance compares favorably to the layer separation tabulated for 21 different crystal structures of aromatic π-donor/acceptor complexes, the average separation being 3.29(6) Å.[25]

In summary, we report that intermolecular π-complexation in HAT hexacarboxamide is induced noncovalently *via* hydrogen bonding. Inasmuch as the manufacturing of desirable macroscopic properties may be derived from engineering at the molecular level, application to other solid-state structures may be envisioned.

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Supplementary Material Available: Crystal structures of compounds **3** and **4** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[21] While a complete description of hydrogen bonding in form A is currently not possible, the present resolution indicates that the HAT molecule is hydrogen-bonded both within a layer and between layers. Within a layer there is cyclic trimer hydrogen bonding with N–O distance 2.94 Å; between layers there is disordered hydrogen bonding with N–O distance 2.54 Å.

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[23] Hydrogen bond parameters for the bifurcated hydrogen bonds shown in Figure 1, form B, are as follows: amide H–O (acceptor) distances [hydrogen bond lengths] 2.33(4) and 2.21(4) Å, corresponding amide N–O (acceptor) distance 3.160(4) and 2.982(5) Å, respectively, and amide N–H–O (acceptor) angles 151(4) and 164(4)°. The positional and isotropic displacement parameters of the H-atoms were full-matrix least-squares refined. The mean amide N–O (acceptor) distance for the 10 intermolecular hydrogen bonds to O acceptors is 3.00(20) Å, while the mean amide N–H–O (acceptor) angle is 158(6)°.

[24] The mean interplane distance between the HAT rings of adjacent dimers is 3.68(10) Å.

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