The Bicyclic N,N’-Diacylaminal: A New Motif for Molecular Self-Assembly

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The principles governing noncovalent self-assembly have been studied intensely recently because of their potential relevance to nanotechnology.1–3 There remains a need to develop new “supramolecular synthons” that can be used to create supramolecular structures with novel three-dimensional architectures. We now report a new molecular recognition motif, the bicyclic N,N’-diacylaminal (“amidal”). In the solid state, the amidals described here self-assemble into either “supramolecular chair cyclohexanes” occupied by two aromatic solvent molecules or infinite tapes. The amide dimers sustaining these supramolecular structures are not coplanar, making these structures uniquely three-dimensional.

We have recently reported tricyclic amidals 1 and 2 (eq 1).4

Amidal 1 crystallizes from toluene, chlorobenzene, and benzotrifluoride in the triclinic space group P1 in the stoichiometry (1)1 (solvent) (mps 197–199 °C). Only minor differences (mostly involving the CO2Et groups) distinguish the three types of 1 within each crystal, and the three (1) sets of the three crystals are nearly superimposable. In each crystal, six amidals (each independent molecule and its enantiomer) self-assemble into a squat cylindrical hexamer occupied by two aromatic guests (Figures 1 and 2). Each monomer makes two hydrogen bonds to each of its neighbors, and the vertical orientation of the amidals alternates around the hexamer, endowing the hexamer with approximate D6d and exact C1 symmetry. The cavities of the hexamers are lined at the top and bottom by the CH3CH2 groups of 1 and in the middle by the CONH groups. The hexamers stack to form six-sided straws occupied by aromatic solvent. These straws are close-packed into roughly hexagonal arrays, like bundles of pencils. The approximate D6d symmetry of the hexamers allows them to be regarded as supramolecular analogues of chair-shaped cyclohexane. The only previously reported “supramolecular chair” is sustained by C−H⋯π interactions and lacks an occupant.5 By contrast, our chairs are sustained by more robust amide dimers, and, in each chair, two arenes sit locked in intimate embrace.

The volumes of the interiors of the cylinders in the three crystals, computed by subtracting the atomic volumes of the atoms making up the cylinders from the volume of the unit cell,6 are approximately 340, 330, and 342 Å3, respectively, at room temperature. (Each pair of guests is calculated to occupy 282, 272, and 319 Å3, respectively, at room temperature. Only in (1)6(C6H5CF3)2 is the volume of the cylinder occupied fully by the guests; in the others, the excess space is evident from the increased thermal motion of the guests.

In (1)6(C6H5Cl)2, the two guests are arranged in a face-to-face and CH1-to-center orientation, whereas in (1)6(C6H5Cl)2 and (1)6(C6H5CF3)2, they are arranged in a face-to-face and edge-to-edge orientation. These observations can be explained by the attractive nature of the CH3−arene interaction and the repulsive nature of the Cl− and CF3−arene interactions. Still, the spaces occupied by the solvent molecules in the two crystals coincide fairly closely, as one would expect.

To our knowledge, the solid-state structures of 1 are the first examples of nonplanar cyclic hexamers held together by R3(8)7-type hydrogen bonds (carboxylic acid dimers, amide dimers, and the like).8 In related work, spherical calixarene hexamers held together only by hydrogen-bonded OH groups and H2O molecules have been reported,9 and a hexamer held together by pyridine-alcohol hydrogen bonds and consisting of two different units has been shown to encapsulate two molecules of nitrobenzene.10 Glycoluril groups, which resemble the bicyclic amidal present in 1 (Figure 3), are assembled into a cylindrical hexameric structure

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Notes:

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2. A 3D rotatable image in MOL format is available.

3. A 3D rotatable image of (1)6(C6H5Cl)2 and (1)6(C6H5CF3)2 in MOL format are available.

4. Figure 1. Views of (1)6(C6H5)2 down a pseudo-C2 axis (left) and the S2 axis (right). Only NH hydrogens and major conformers of disordered CO2Et groups are shown for clarity. O, red; C, gray; N, blue; H, white.

5. Figure 2. View of (1)6(C6H5Cl)2 (left) and (1)6(C6H5CF3)2 (right) down pseudo-C2 axes. Only NH hydrogens and major conformers of disordered CO2Et groups are shown for clarity. Halogens are green.

6. View of (1)6(C6H5Cl)2 (left) and (1)6(C6H5CF3)2 (right) down a pseudo-C2 axis. Only NH hydrogens and major conformers of disordered CO2Et groups are shown for clarity. Halogens are green.

7. To a planar cyclic hexamer held together by R3(8)7-type hydrogen bonds (carboxylic acid dimers, amide dimers, and the like).

8. In related work, spherical calixarene hexamers held together only by hydrogen-bonded OH groups and H2O molecules have been reported, and a hexamer held together by pyridine-alcohol hydrogen bonds and consisting of two different units has been shown to encapsulate two molecules of nitrobenzene. Glycoluril groups, which resemble the bicyclic amidal present in 1 (Figure 3), are assembled into a cylindrical hexameric structure.
via R(8)-type hydrogen bonds in Rebek’s dimeric “jelly doughnut,” but in this compound alternate glycolurils are covalently held in the orientations necessary for formation of the cylinder. The same is true for de Mendoza’s dimeric triureidocalix[6]arenes, which are held together by R(6)-type hydrogen bonds.

By contrast, the self-assembly of the cyclic hexamers of 1 requires the organization of six separate molecules per hexamer.

Amidal 1 also crystallizes from C₆H₅NO₂ and C₆H₆, but in the stoichiometry 1(solvent); it also crystallizes from heptane-CH₂Cl₂(2,2)-type hydrogen bonds, but to form infinite tapes instead of hexamers (Figure 4). Infinite tapes sustained by R(8)-type hydrogen bonds are common, but those in which the hydrogen-bonded units are not coplanar are rare. The nonplanarity of the hexamers of 1 is reminiscent of that of 1,3-cyclohexanedione, which crystallizes from nitrobenzene. Only one independent molecule of 1 grown from nitrobenzene. Only one independent molecule of 1

The nonplanarity of the hexamers of 1 has implications for the synthesis of topologically complex, three-dimensional supramolecular architectures. Conceivably, amidals with varying dihedral angles and substitution patterns would self-assemble in other interesting ways. The ability to control the solid-state structure of 1 with the crystallization solvent also creates interesting possibilities for supramolecular synthesis. The easy syntheses of 1 and 2 bode well for the preparation of other self-assembling monomers based on the bicyclic amidal motif. Future work will explore just how general is this assembly motif, whether two guests can be induced to undergo unusual reactions, and the design of molecular recognition devices based on the bicyclic amidal.

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Supporting Information Available: Details of the X-ray studies of 1 and 2 (PDF). An X-ray crystallographic file is available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(16) Even larger and more complex assemblies have been prepared by pairing two different molecules with complementary shapes. Jolliffe, K. A.; Timmerman, P.; Reinhardt, D. N. Angew. Chem., Int. Ed. 1999, 38, 993 and references therein.