Supramolecular organization of extended benzobisoxazole cruciforms†

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Extended benzobisoxazole-based cruciforms, efficiently synthesized using acyl condensations and Sonogashira couplings, form highly ordered two-dimensional sheets in the solid state.

Molecular cruciforms1 constitute a class of cross-conjugated π-systems characterized by rigid X-shaped geometry with two conjugation circuits intersecting at the central aromatic core. In these compounds, appropriate substitution can localize the HOMO and the LUMO on different portions of the molecule, boding well for applications in sensing2 and molecular electronics.3 Given their rigid geometries, cruciforms represent intriguing crystal engineering synthons. However, relatively little attention has been paid to the crystal packing of molecular cruciforms, despite several reported crystal structures.2c,3c,4 In this Communication, we describe the synthesis of extended benzobisoxazole-based cruciforms 1–3 (Fig. 1) and their organization into highly ordered (2D) sheets in the solid state.

Pioneering studies of benzobisoxazole† cruciforms have been performed by Nuckolls and coworkers,1,6,3 yielding the first crystal structure of a benzobisoxazole substituted with four rigid (phenyl) groups.3e Inspired by this work, we initiated an effort to prepare benzobisoxazole cruciforms substituted with carboxylic acid groups5 and organize them into 2D and 3D superstructures through either hydrogen-bonding –COOH dimers6 or as components of MOFs.7 During the course of these studies, we were delighted to discover that synthetic intermediates 2 and 3 form highly ordered 2D arrays in the crystalline state, despite the fact that they have no functionalities capable of strong supramolecular association.

Compounds 1–3 are characterized by two perpendicular molecular axes: the *bisethynylbenzene axis* (vertical in Fig. 1) and the *benzobisoxazole axis* (horizontal in Fig. 1), which can be elaborated independently. The syntheses of 1–3 (Scheme 1) commenced with 2,5-diamino-3,6-dibromobenzene-1,4-diol (4).8 Microwave-assisted condensation9 of 4 with ethyl chloroglyoxylate provided compound 5 in 20% yield, while the analogous reaction with 4-cyanobenzoyl chloride gave 6 in 78% yield. Bisethynylbenzene axes were then introduced into 5 and 6 using Sonogashira coupling:10 reaction of 5 with 2 equiv. of ethyl 4-ethynylbenzoate gave 1 in 96% yield, while the use of longer terminal alkyne ethyl-

4-[(4-ethynylphenyl)ethynyl]benzoate gave 2 in 81% yield (see ESI for structures of terminal alkyne precursors and synthetic details†). Reaction of 6 with ethyl 4-ethynylbenzoate afforded 3 in 93% yield.

Compounds 1–3 are bright yellow powders, with intense fluorescence in solution and moderate solubility in common organic solvents. The identities of all new compounds have been confirmed by mass spectrometry and by NMR (1H and 13C), IR, and UV-Vis spectroscopies.

Slow cooling of saturated CH2Cl2 solutions of esters 2 and 3 produced needle-shaped crystals suitable for X-ray diffraction.§ Both 2 and 3 crystallize in the P1 space group, with respective asymmetric units containing half a molecule of 2 or 3 and one disordered molecule of CH2Cl2.

In the solid state, molecules of 2 (Fig. 2) are oriented around an inversion center, with the disorder in the benzobisoxazole core making oxazole nitrogens and oxygens indistinguishable. The molecule is largely planar, with significant deplanarization...
occurring in the pendant ethyl groups and the terminal benzene ring, which is twisted out of the central molecular plane by 24.8°. Molecules of 2 assume an undulating conformation with an angle of 167.8° between the centroids of three benzene rings. This shape is brought about by the synergistic distortion of all triple bonds, with C\_\_C–C angles in the 173.8–178.2° range. Molecules of 2 orient parallel to each other in the solid state (Fig. 2B), forming a strikingly ordered 2D sheet. The –COOEt groups on the benzo-bisoxazole axes of 2 engage in pairwise short [C–H/C\_\_C/C\_\_C/O] contacts11 with adjacent molecules (contact 1 in Fig. 2A), with an H/C\_\_C/C\_\_C/O distance of 2.44 Å. The –COOEt groups on the bisethynylbenzene axis establish [C–H/C\_\_C/C\_\_C/O] contacts with the aryl hydrogens of adjacent molecules (contact 2 in Fig. 2A), characterized by a slightly longer H/C\_\_C/C\_\_C/O distance of 2.53 Å.

The solid state structure of 3 (Fig. 3) also reveals a planar central core and deplanarized terminal benzene rings on the bisethynylbenzene axis, twisting out of plane by 27.1°. Each molecule of 3 engages in sixteen intermolecular non-solvent short contacts, four of which are symmetry-unique: (1) a [C–H⋅⋅⋅O=C] contact between the ester carbonyl oxygen and the hydrogen ortho- to the –CN group (contact 1 in Fig. 3A), (2) a [C–H⋅⋅⋅N=C] contact between the cyano nitrogen and the other hydrogen ortho- to the –CN group (contact 2 in Fig. 3A), and (3)/(4) a bifurcating pair of [C–H⋅⋅⋅N=C] contacts established between the ester CH\_\_ group and the –CN group (contacts 3 and 4 in Fig. 3A, see caption for distances and angles).12 Overall, molecules of 3 pack parallel to each other into a well-ordered 2D network (Fig. 3B).

Based on geometric parameters, it has been suggested13 that short [C–H⋅⋅⋅X] contacts, analogous to those observed in the structures of 2 and 3, could be interpreted as weakly stabilizing [C–H⋅⋅⋅X] hydrogen bonds. At present, we feel that further crystallographic studies of analogs of 2 and 3 are needed to distinguish between a genuine interaction and an artefact of crystallographic close packing. Unfortunately, the extensive overlap of C–H vibrations with other bands in the IR spectra of 2 and 3 prevented us from gathering spectroscopic insight into these potential hydrogen bonds.

In summary, we have synthesized a series of extended π-conjugated cruciforms based on the benzoazole nucleus. Two crystallographically characterized examples form remarkably ordered 2D sheets in the solid state, characterized by a number of close [C–H⋅⋅⋅O] and [C–H⋅⋅⋅N] contacts. Our current efforts are directed toward establishing whether these packing patterns are general.

Scheme 1 Synthesis of cruciforms 1–3. Conditions: (a) ethyl 4-ethynyl-benzoate/PdCl\_\_PPh\_\_Cul/NEt\_\_jwave/120 °C/45–60 min; (b) ethyl 4-[(4-ethynylphenyl)ethynyl]benzoate/PdCl\_\_PPh\_\_Cul/NEt\_\_jwave/120 °C/45 min.

Fig. 2 (A) Crystal structure of 2 with short intermolecular contacts highlighted in green. Contact 1: H⋅⋅⋅O 2.44 Å, C⋅⋅⋅O 3.32 Å, C–H⋅⋅⋅O 138.1°, C–O⋅⋅⋅H 151.3°. Contact 2: H⋅⋅⋅O 2.53 Å, C⋅⋅⋅O 3.43 Å, C–H⋅⋅⋅O 139.3°, C–O⋅⋅⋅H 123.3°. (B) Compound 2 packs into corrugated two-dimensional sheets that organize into three-dimensional structure through [π⋅⋅⋅π] stacking. Solvent molecules are omitted. C—gray, H—white, N—blue, O—red.
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Notes and references

† In this Communication, “benzobisoxazole” will signify “benzo-[1,2-d:4,5-d′]bisoxazole” — the systematic name for the central heterocyclic core of 1–3, 5, and 6.

‡ CCDC 768804 (2) and CCDC 768803 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.


5 Results of these investigations will be reported elsewhere.


