Concomitant polymorphism and supramolecular isomerism in 1,3,5-tris(4-cyanobenzoyl)benzene

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L e t t e r

The title compound, 1,3,5-tris(4-cyanobenzoyl)benzene, exhibits the phenomenon of concomitant polymorphism. Two distinct isomeric solid-state networks, honeycomb and ladder, were obtained upon crystallization from acetone–water solution. Conformational flexibility of the molecule appears to facilitate polymorph formation. Each network is maintained *via* formation of multiple C–H···N and C–H···O hydrogen bonds.

A molecule that adopts more than one distinct packing arrangement in the solid state is said to be polymorphic.[1] The occurrence of polymorphs implies that the free energies of the various crystalline forms are comparable.[2] Polymorphism is important across a wide range of industries in which the properties and/or performance of various products are a function of structure. Reproducibly obtaining a specific polymorph of a given compound can be a critical issue for the proper formulation of pharmaceuticals, dyes, explosives and pigments.[3] Polymorphism results when different (but energetically similar) packing interactions are operative during crystal growth. With rigid molecules, polymorphism is manifested through different packing motifs. With flexible molecules, different low-energy conformational arrangements can give rise to polymorphic modifications (*i.e.*, conformational polymorphs). Indeed, in conformationally flexible molecules, the energies required to rotate about single bonds are comparable in magnitude to the lattice energy differences observed between polymorphs.[4] Consequently, a greater tendency to exhibit polymorphism might be expected for conformationally flexible molecules.[5] For example, nineteen independent conformations of the same molecule were found in the tetramorphic cluster of 4,4-diphenyl-2,5-cyclohexadienone.[6] Materials that form crystalline polymer networks in which individual molecules are connected *via* discrete intermolecular interactions also exhibit polymorphism. In these instances, polymorphic forms result in different network superstructures, and the terms supramolecular isomerism[7] and architectural isomerism[8] have been coined to describe these systems.

Visualization of organic crystal structures as networks with molecules acting as nodes and supramolecular synthons as node connectors facilitates retrosynthetic analysis in the context of crystal engineering applications.[9–11] In particular, the self-assembly of honeycomb, brick wall, ladder, bilayer and herringbone networks from purely organic as well as metal-organic building blocks is currently under active investigation.[7,9b] The design of such network structures may be traced to three-connected scaffolds in the retrosynthetic sense (Scheme 1). These networks are topologically identical and self-assembly is controlled by supramolecular isomerism. Honeycomb networks derived from three-connected building blocks are commonly encountered in crystal structures of organic
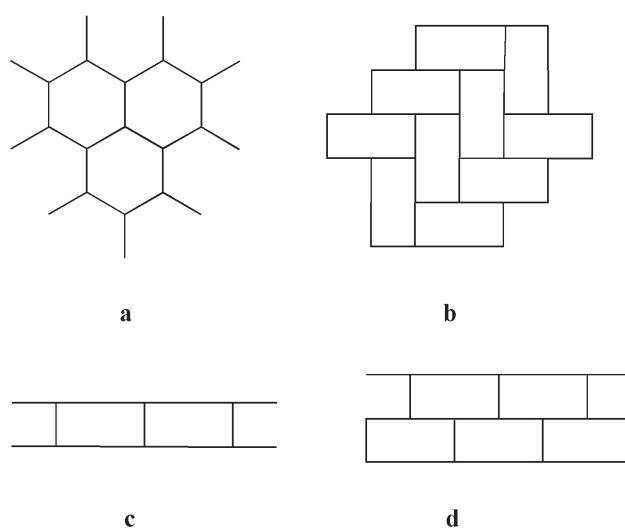
Scheme 1 Examples of three-connected networks: (a) honeycomb; (b) herringbone; (c) ladder; (d) brick wall.

compounds,[12] but there are fewer examples of coordination polymers that exhibit this network topology.[7,13] On the other hand, brick wall, ladder, herringbone, and bilayer networks are rarely observed in organic crystals,[14] but they are relatively common in coordination polymers.[7,15] Here we describe two X-ray crystal structures of 1,3,5-tris(4-cyanobenzoyl)benzene (**1**), a material that exhibits concomitant polymorphism[16] and conformational polymorphism[17] in the same system. The dimorph **1** also provides an example of supramolecular isomerism through assembly of discrete honeycomb and ladder networks.[18]

As a part of ongoing studies aimed at defining the inclusion host properties of substituted 1,3,5-triaroylbenzenes[19] and determining the ability of functionalized triaroylbenzenes to mediate the formation of metal-organic coordination polymers,[20] the title compound 1,3,5-tris(4-cyanobenzoyl)benzene (**1**) was prepared (Scheme 2). Recrystallization of **1** from 1:1 acetone–water solution afforded two concomitant polymorphs (forms **A** and **B**) as revealed by low temperature single-crystal X-ray diffraction. The two crystallographically independent

Scheme 2

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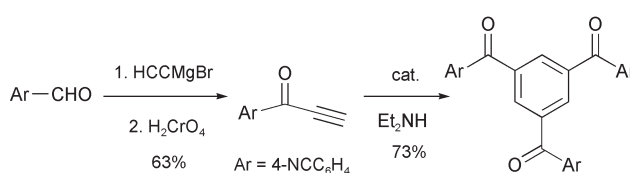
molecules observed in the dimorphs of **1** differ in the rotation about the C–C bonds between the cyanobenzoyl groups and the central 1,3,5-substituted benzene ring. These conformations may be defined according to the three torsion angles τ_1, τ_2 and τ_3 (Table 1). Conformational changes from one structure to the other leads to the formation of two different polymorphs; hence, these concomitant polymorphs also may be described as conformational polymorphs.[17]

Each polymorph exhibits a distinct network structure mediated by weak solid-state hydrogen bonding interactions. In form **A**, each roughly Y-shaped molecule of **1** has three pairs of donor/acceptor sites that participate in intermolecular hydrogen bonding.[21] Two of the three sites are adjacent and interact with a complementary array of sites on a neighboring molecule, thereby resulting in four contiguous hydrogen bonds. Two approximately co-planar carbonyl oxygens and two phenyl hydrogens form a centrosymmetric four point recognition pattern through two unique C–H⋯O hydrogen bonds (d, θ: 2.43 Å, 169.8°; 2.61 Å, 138.8°). The other two nodes of the three-connected molecules extend through C–H⋯N centrosymmetric dimers involving phenyl hydrogens and nitrile acceptors (2.77 Å, 123.7°; 2.78 Å, 125.5°). Thus the three-connected molecule produces a honeycomb network as shown in Fig. 1. The central benzene ring and two cyanobenzoyl rings participate in network formation. The third cyanobenzoyl ring fills the hexagonal void formed in the network to avoid an open structure. Additional hydrogen bonding between this nitrile group and a phenyl hydrogen within the void (2.50 Å, 156.3°) further stabilizes the structure.

Form **B** has similar cell dimensions but differs slightly in volume as compared to form **A**. The solid-state network in form **B** consists of centrosymmetric C–H⋯N hydrogen bond dimers (2.56 Å, 137.4°) similar to those encountered in form **A** but involving a different aryl hydrogen bond donor (Fig. 2). The other two nodes of the three-connected T-shaped building blocks extend *via* C–H⋯N interactions (2.32 Å, 163.7°) involving translation related molecules to furnish a ladder network. The inversion related ladders are connected *via* C–H⋯O hydrogen bond dimers (not shown in Fig. 2). The conformation of **1** is slightly different in the two polymorphs, and this presumably accounts for the dramatic change in network architecture. While supramolecular isomerism has been observed in other crystalline networks,[7,14c–d,18] examples of concomitant supramolecular isomerism appear to be less common.[22]

The relative stability of the two polymorphs has not been determined. Because these are concomitant polymorphs of similar crystalline morphology (*i.e.*, visually indistinguishable), separation of the two forms was not possible. The solid-state structures, however, would appear to indicate that form **A** is
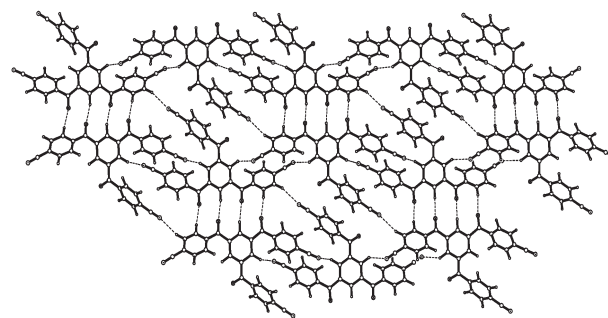

Fig. 1 Crystal structure of form **A**. Note each molecule is connected to three inversion related neighbors to produce the honeycomb network. Hydrogen bonds are shown as dashed lines.
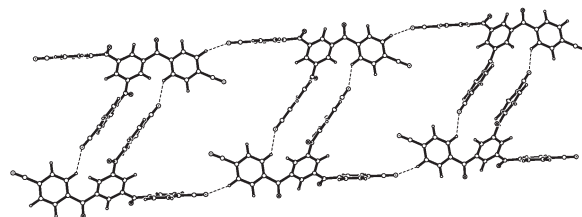

Fig. 2 Ladder network observed in form **B**.

the lower energy modification. This assertion is based on the observation that almost all of the hydrogen bonding acceptor sites (carbonyl oxygens and nitrile nitrogens) are engaged in intermolecular interactions in the honeycomb structure shown in Fig. 1. In contrast, fewer solid-state hydrogen bonds are present in form **B**. Consequently, form **A** exhibits closer crystal packing than form **B**, thus resulting in a smaller crystal volume. Additionally, the calculated density of form **A** is greater than that of form **B** (1.384 *vs.* 1.352 g cm^{-3}, respectively).

In summary, two concomitant conformational polymorphs of cyano-substituted 1,3,5-triaroylbenzene derivative **1** have been structurally characterized. The conformational flexibility of **1** coupled with the large number of potential hydrogen bond donor and acceptor sites undoubtedly contribute greatly to the observed polymorphism. In both crystalline forms, solid-state C–H⋯N and C–H⋯O hydrogen bonds propagate isomeric supramolecular networks. Triaroylbenzenes have previously been shown to act as crystalline inclusion hosts[19] and to participate in the assembly of metal-organic coordination polymers.[20] The results of the present study indicate that this readily accessible molecular framework may also prove useful in further exploring the phenomenon of polymorphism. Work along these lines continues and results will be reported in due course.

Experimental

Compound **1** was synthesized from *p*-cyanobenzaldehyde as previously described.[20] X-ray quality crystals of the concomitant polymorphs were obtained by slow evaporation of a 1:1 acetone–water solution at ambient temperature. Both crystalline modifications were found to be present as evidenced by X-ray diffractometry (Figs. 1 and 2). Random selection of additional single crystals and determination of unit cell constants at 165 K also revealed the presence of both forms.

Crystal data

Preliminary examination and data collection was performed using a Bruker SMART CCD area detector system single crystal X-ray diffractometer. The SHELXTL-PLUS software

Table 1 Torsion angles observed in the dimorphs of **1**
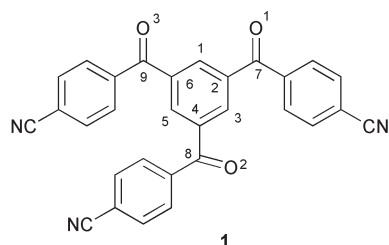
Polymorph	τ_1 (C1–C2–C7–O1) [deg]	τ_2 (C3–C4–C8–O2) [deg]	τ_3 (C5–C6–C9–O3) [deg]
Form **A**	39.2(2)	146.1(2)	36.8(3)
Form **B**	27.7(3)	164.9(2)	17.3(2)

package was used for structure solution and refinement.[23] Hydrogens were fixed at idealized geometries and treated isotropically as riding groups.

Form **A:** Triclinic, $P\bar{1}$, $a = 5.9762(2)$, $b = 13.9047(4)$, $c = 14.2152(4)$ Å, $\alpha = 71.790(2)$, $\beta = 84.290(2)$, $\gamma = 87.967(2)°$, $V = 1116.51(6)$ Å^3, $Z = 2$, $D_c = 1.384$ g cm^{-3}, $T = 200$ K, $F(000) = 480$ $\lambda = 0.71073$ Å, $\mu = 0.091$, $R1 = 0.0530$ for 3708 $Fo > 2\sigma(Fo)$, $wR_2 = 0.1361$ for 5486 independent reflections. CCDC reference number 215270.†

Form **B:** Triclinic, $P\bar{1}$, $a = 7.7072(2)$, $b = 11.3057(2)$, $c = 13.7913(2)$ Å, $\alpha = 73.284(1)$, $\beta = 88.422(1)$, $\gamma = 83.420(1)°$, $V = 1143.33(4)$ Å^3, $Z = 2$, $D_c = 1.352$ g cm^{-3}, $T = 165$ K, $F(000) = 480$ $\lambda = 0.71073$ Å, $\mu = 0.089$, $R1 = 0.0445$ fo $Fo > 2\sigma(Fo)$, $wR_2 = 0.1084$ for 4900 independent reflections. CCDC reference number 215271.†

Acknowledgements

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