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The potential of intermolecular N···O interactions of nitro groups in crystal engineering, as revealed by structures of hexakis(4-nitrophenyl)benzene

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Dedicated on the occasion of the 50th anniversary of *Tetrahedron* to the memory of its founding editors, Sir Robert Robinson and Robert Burns Woodward

Abstract—Like other derivatives of hexaphenylbenzene, hexakis(4-nitrophenyl)benzene (**1**) crystallizes under a variety of conditions as layered structures in which significant quantities of guests are included in spaces between the layers or within them. In structures of nitroarene **1**, multiple intermolecular N···O interactions of NO_2 groups help to hold the layers together and determine how the molecular constituents are positioned. The behavior of nitroarene **1** confirms that N···O interactions can allow crystal engineers to position molecules with a useful degree of predictability, particularly when stronger interactions such as hydrogen bonds are absent, and when competition with other weak interactions is limited.

1. Introduction

No current methods allow the structures and properties of new molecular crystals to be predicted reliably.[1] This constitutes a significant obstacle to progress in materials science and technology. Developing suitable predictive methods is a key goal of the rapidly growing field of crystal engineering.[2] Although this goal has not yet been reached, the ability to control molecular crystallization is increasing dramatically. In part, this progress has occurred because crystal engineers have taken advantage of impressive new tools, including advanced theoretical approaches, accelerated generation of crystallographic data, perceptive statistical analyses of collections of structures, revolutionary methods for revealing crystalline surfaces at atomic resolution, and powerful modern techniques for designing and synthesizing promising molecules.

A productive strategy for engineering new crystals is based on treating them as supramolecular constructs held together by particular intermolecular forces. If each molecular component participates in multiple interactions that are strong and directional, then subsequent association will favor the creation of networks in which each component is positioned predictably with respect to its neighbors. In this strategy of programmed molecular construction, proper choice of the individual components (which have been called tectons[3]) and their patterns of interaction (which have been called supramolecular synthons[4]) allows crystal engineers to come very close to the goal of producing new structures with predetermined features.[5] This strategy is expected to be most effective when (1) the tectons have well-defined structures, such as those provided by relatively rigid molecular cores and (2) reliable supramolecular synthons are used, such as those involving multiple classical hydrogen bonds. Nevertheless, useful degrees of control can be attained even when the tectons have significant flexibility[6] or when the intermolecular interactions are weaker and less directional.[7]

In exploring the potential of weaker supramolecular synthons, crystal engineers and structural chemists have begun to pay special attention to interactions of the NO_2 group.[8–20] In part, this interest reflects the central role of nitro compounds in molecular synthesis, their significant electron-withdrawing electronic effects, and the variety of supramolecular synthons in which they can engage. Figures 1 and 2 present selected intermolecular interactions observed in structures of simple nitroarenes. In motifs **I–III** (Fig. 1), the NO_2 group serves as an acceptor of a C–H···O hydrogen bond;[7] in motifs **IV–VI** (Fig. 2), N···O interactions involving two or more NO_2 groups are present;[11–16] and in motif **VII** (Fig. 2), dispersive interactions are involved.[17] Related

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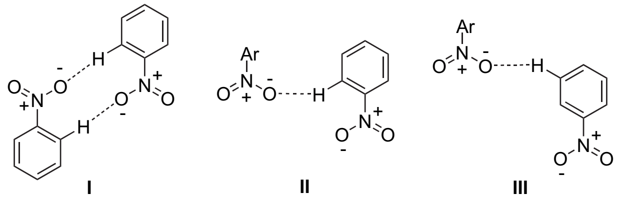


Figure 1. Selected C–H···O interactions involving nitroarenes.

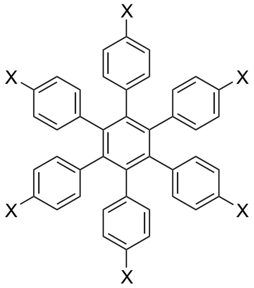
N···N or N···O interactions involving an NO_2 group and a different partner have also been observed.[18,19] In addition to these selected interactions of NO_2 groups,[20] the aryl groups of nitroarenes can also engage directly in characteristic aromatic interactions.

Assessing the relative importance of weak interactions of NO_2 groups is difficult, but several useful guidelines have emerged:

1. NO_2 groups are intrinsically poorer acceptors of hydrogen bonds than related groups with greater electron density on oxygen, such as nitrones or carboxylates.[10,21]
2. The tendency of nitroarenes to adopt conformations with coplanar NO_2 groups and aryl rings can disfavor the in-plane approach of hydrogen–bond donors and lead to distortions in bond angles.[22]
3. Calculations have revealed that N···O interactions of NO_2 groups can be at least as strong as C–H···O hydrogen bonds.[12]
4. Theoretical studies have concluded that dispersive interactions such as motif **VII** (Fig. 2) are stronger than electrostatic attractions involving NO_2 groups.[17]

These guidelines suggest that N···O interactions of NO_2 groups may play a key role in determining how nitroarenes crystallize when they cannot engage in stronger intermolecular interactions such as classical hydrogen bonds, and when the opportunity to participate in alternative weak interactions is restricted. However, previous studies on the potential of NO_2 groups in crystal engineering have provided few examples in which N···O interactions can be considered to make a dominant contribution to molecular adhesion and organization.[15]

Recent studies of the crystallization of derivatives of hexaphenylbenzene[23–26] led us to examine the behavior of the NO_2 groups of hexakis(4-nitrophenyl)benzene (**1**).[27] Like other hexaphenylbenzenes, nitroarene **1** is expected to favor a chiral propeller conformation and to have a disc-shaped geometry that induces the formation of layered structures.[23–26] The complex molecular geometry should disfavor extensive intermolecular aromatic interactions, as well as C–H···O interactions of NO_2 groups involving relatively inaccessible *meta* hydrogens (motif **III**, Fig. 1) or dispersive interactions requiring close contact of hexaphenylbenzene cores (motif **VII**, Fig. 2). Moreover, the tendency to form layered structures assembled from disc-shaped components should inhibit the formation of cyclic doubly hydrogen-bonded motifs in which the *ortho* hydrogens of nitroaryl groups participate (motif **I**, Fig. 1). Geometric constraints imposed by the hexaphenylbenzene core of nitroarene **1**, together with the absence of groups that can take part in classical hydrogen bonds, therefore suggest that crystallization will be controlled by the following limited set of NO_2 interactions: single C–H···O interactions involving primarily *ortho* hydrogens (motif **II**, Fig. 1), N···O interactions (motifs **IV–VI**, Fig. 2), or other cyclic oligomeric motifs analogous to structures **V** and **VI**.



1 (X = NO_2)
2 (X = CN)

In this paper, we report the synthesis of nitroarene **1**, its characterization, and the structure of crystals obtained under six different conditions. Analysis of the structures establishes that (1) compound **1** favors layered structures, as expected, and therefore behaves like a typical hexaphenylbenzene; (2) the dominant intermolecular interactions within the layers are N···O interactions of NO_2 groups; and (3) in certain cases, the layers are joined to adjacent layers of nitroarene **1** by C–H···O interactions according to motifs **I** and **II** (Fig. 1), or they are simply separated by intervening layers of included solvent.

2. Results and discussion

2.1. Synthesis of hexakis(4-nitrophenyl)benzene (1)

Nitroarene **1** was first described in 1971 by Bergmann in a brief communication that reported only its decomposition point and elemental analysis.[27] We obtained the compound

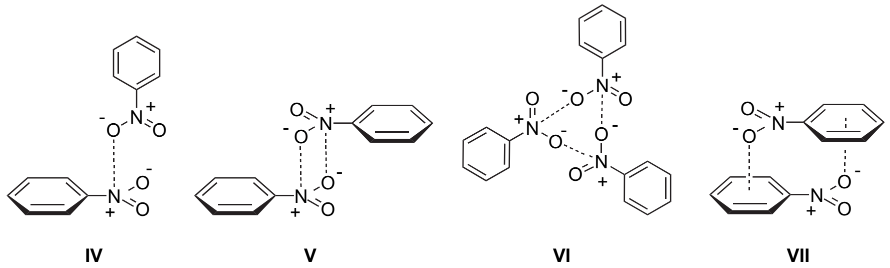


Figure 2. Selected N···O (**IV–VI**) or dispersive (**VII**) interactions involving nitroarenes.

by the direct nitration of hexaphenylbenzene[28] in fuming HNO_3 containing a catalytic amount of H_2SO_4. Subsequent crystallization of the crude product from DMSO gave purified nitroarene **1** in 60% yield.

2.2. Crystallization of hexakis(4-nitrophenyl)benzene (1)

Crystals suitable for structural studies by X-ray diffraction were obtained by allowing vapors of suitable cosolvents to diffuse into solutions of nitroarene **1** in *N*,*N*-dimethylformamide (DMF). Crystallographic data are summarized in Table 1.

2.2.1. Structure of crystals of hexakis(4-nitrophenyl)-benzene (1) grown from DMF/benzene. Crystals grown by allowing vapors of benzene to diffuse into solutions of nitroarene **1** in DMF were found to belong to the triclinic space group $P\overline{1}$ and to have the composition **1**·7 benzene, as established crystallographically (Table 1). Included benzene occupies 54% of the volume of the crystals, and no included DMF is observed (Table 2). Derivatives of hexaphenylbenzene are known to define a class of compounds with molecular shapes that disfavor efficient packing in crystals, and guests are included in essentially every previously reported structure.[23–26] In crystals in which the inherent difficulties of packing hexaphenylbenzenes have been exacerbated by forcing them to engage in strong directional intermolecular interactions, the percentage of volume accessible to guests can even exceed 70%.[24] The observed inclusion in crystals of compound **1** is therefore fully consistent with the general behavior of derivatives of hexaphenylbenzene.

As expected, molecules of nitroarene **1** lie in well-defined monolayers and adopt a chiral propeller-shaped conformation, as observed in many other derivatives of hexaphenylbenzene.[23–26] The torsional angles between the central and outer rings have values in the range 63–71° (Table 3), and each layer of nitroarene **1** contains an equal number of the two enantiomers. Each molecule is linked to six neighbors within the same layer by multiple N···O interactions of NO_2 groups, which can be considered to be the principle force ensuring adhesion of the layers (Fig. 3).

Table 2. Summary of key structural features observed in pseudopolymorphs of hexakis(4-nitrophenyl)benzene (**1**)

Composition	Volume occupied by guests (%)	Number of adjacent molecules of nitroarene **1** engaging in significant N···O interactions[a,b]	Total number of significant N···O interactions per molecule[b]
1·7 benzene	54	6	12
1·7 dioxane	52	4	8
1·2 acetonitrile	18	4	16
1·2 acetone	19	4	12
1·2 ethanol	14	4	12
1·2 DMF	22	4	12

[a] As measured per molecule of nitroarene **1**.

[b] Significant N···O interactions are judged to be those shorter than 3.5 Å.[11,12]

In accord with the criterion adopted by Woźniak et al.,[11,12] N···O interactions are judged to be significant if the distance is less than 3.5 Å. Bonding would normally require an N···O distance of less than 3.07 Å,[29] which corresponds to standard values for the van der Waals radii of oxygen (1.52 Å) and nitrogen (1.55 Å); however, the dipolar character of NO_2 groups allows their N···O interactions to be significantly stabilizing at distances exceeding the sum of the van der Waals radii. In the structure of crystals grown from DMF/benzene, each molecule of nitroarene **1** engages in 12 interactions that satisfy this criterion by lying in the range 3.153(4)–3.410(4) Å. Of these interactions, six are incorporated in a set of three cyclic trimers (motif **VI**, Fig. 2). Related

Table 3. Conformations adopted by the hexaphenylbenzene core of nitroarene **1** in different pseudopolymorphs

Included guest	Angles (°) between the average planes of the 4-nitrophenyl substituents and the central ring of the hexaphenylbenzene core
Benzene	60.99(12), 63.61(12), 63.92(13), 67.91(12), 68.05(12), 70.46(13)
Dioxane	81.81(12) (2×), 84.29(10) (2×), 87.87(11) (2×)
Acetonitrile	60.83(11), 62.61(11), 65.70(9) (2×), 67.80(9) (2×)
Acetone	62.10(8), 63.11(9) (2×), 64.23(9) (2×), 67.64(7)
Ethanol	71.46(17) (2×), 78.99(18) (2×), 79.11(15) (2×)
DMF	73.1(3), 73.9(4), 76.3(3), 82.0(3), 84.8(3), 88.7(3)

Table 1. Crystallographic data for pseudopolymorphs of hexakis(4-nitrophenyl)benzene (**1**)

Included solvent	7 Benzene	7 Dioxane	2 Acetonitrile	2 Acetone	2 Ethanol	2 DMF
Formula	$C_{84}H_{66}N_6O_{12}$	$C_{70}H_{80}N_6O_{26}$	$C_{46}H_{30}N_8O_{12}$	$C_{48}H_{36}N_6O_{14}$	$C_{46}H_{36}N_6O_{14}$	$C_{48}H_{38}N_8O_{14}$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	*C*2/*c*	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$
a (Å)	11.1911(9)	11.533(2)	11.237(2)	11.181(4)	10.7355(10)	11.6772(13)
b (Å)	13.9932(11)	13.037(3)	20.367(5)	20.593(6)	13.9310(14)	17.9809(19)
c (Å)	24.378(2)	14.014(3)	19.002(4)	20.074(5)	14.1161(15)	11.9334(13)
α (°)	84.436(5)	105.10(3)	90	90	90	90
β (°)	83.004(5)	108.37(3)	102.048(11)	104.739(8)	98.039(6)	116.183(6)
γ (°)	68.693(5)	110.42(3)	90	90	90	90
V (Å^3)	3524.5(5)	1703.7(6)	4253.0(16)	4470(2)	2090.4(4)	2248.5(4)
Z	2	1	4	4	2	2
ρ_{calcd} (g cm^{-3})	1.273	1.385	1.385	1.368	1.425	1.404
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ (mm^{-1})	0.697	0.897	0.864	0.862	0.904	0.888
R_1, $I>2\sigma$ (all)	0.0650	0.0567	0.0568	0.0542	0.0665	0.0567
ωR_2, $I>2\sigma$ (all)	0.1465	0.1327	0.1292	0.1670	0.1422	0.1442
Measured reflections	11,726	5328	3815	3217	3774	4938
Independent observed reflections	6567	3740	2069	3878	2110	3946

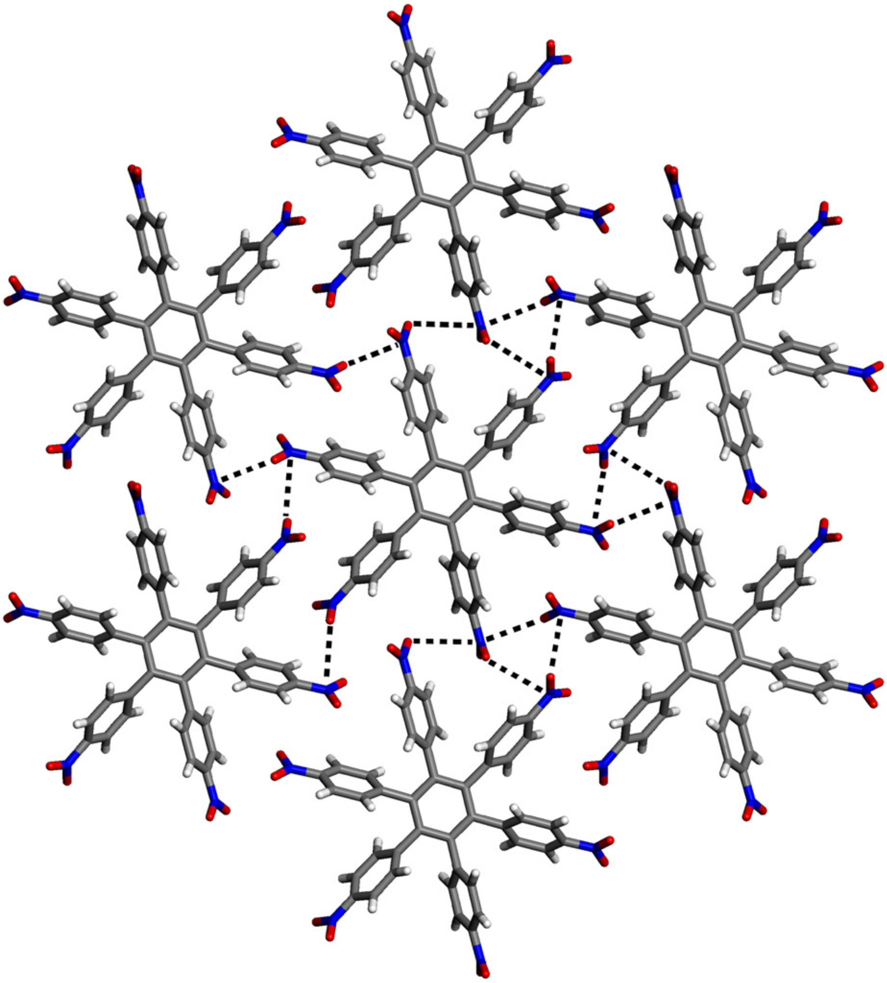


Figure 3. View of the structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/benzene, showing significant N···O interactions (N···O distances <3.5 Å) between NO_2 groups of a central molecule of nitroarene **1** and its six coplanar neighbors. The interactions are represented by broken lines. Atoms of hydrogen appear in white, carbon in gray, nitrogen in blue, and oxygen in red.

trimeric aggregates of NO_2 groups were first explicitly recognized as potential supramolecular synthons by Nangia, Mak, and collaborators;[15] however, similar trimeric motifs are present in the structures of many nitroarenes, although they have frequently been overlooked.[30] In the trimeric motif described by Nangia, Mak, and collaborators,[15] both N···O and O···O interactions appear to be significant, but in the trimeric motifs identified in Figure 3, the average N···O distance is much shorter than the average O···O distance. This suggests that trimeric aggregates of NO_2 groups can adopt distinctly different geometries and should not be regarded as particularly reliable supramolecular synthons.

In the structure of crystals of nitroarene **1** grown from DMF/benzene, monolayers composed of compound **1** are separated by monolayers of included benzene (Fig. 4). Each molecule of benzene is surrounded by six others in the same layer. The characteristic propeller-shaped conformation of hexaphenylbenzene **1** defines a toroidal volume with a central indentation on each face that can partially accommodate a molecule of benzene. Two molecules of benzene from different layers are oriented in such a way that each directs a C–H bond toward the center of the toroidal volumes defined by host **1** (Fig. 4), creating C–H···aromatic interactions with H···centroid distances of 2.58(1) and 2.78(1) Å. There are no important intralayer C–H···O interactions of NO_2 groups, as anticipated, but each molecule of nitroarene **1** engages in multiple C–H···O interactions with molecules of benzene in adjacent layers (H···O distances in the range 2.46(1)–2.74(1) Å).

2.2.2. Structure of crystals of hexakis(4-nitrophenyl)benzene (1) grown from DMF/dioxane. Crystals grown by allowing vapors of dioxane to diffuse into solutions of nitroarene **1** in DMF proved to belong to the triclinic space group $P\overline{1}$ and to have the composition $\mathbf{1}\cdot 7$ dioxane, as determined crystallographically (Table 1). Their structure is closely similar to that of crystals grown from DMF/benzene, and it will not be discussed in detail (see the Supplementary data for figure). Dioxane occupies 52% of the volume, and again no DMF is included (Table 2). Molecules of nitroarene **1** lie in well-defined monolayers and adopt a conformation in which the central and outer rings of the hexaphenylbenzene core are essentially orthogonal, with torsional angles in the range 81–88° (Table 3). Each molecule of nitroarene **1** is joined to neighbors within the same layer by eight significant N···O interactions (four N···O distances of 3.396(3) Å and four distances of 3.461(3) Å). These interactions are all of

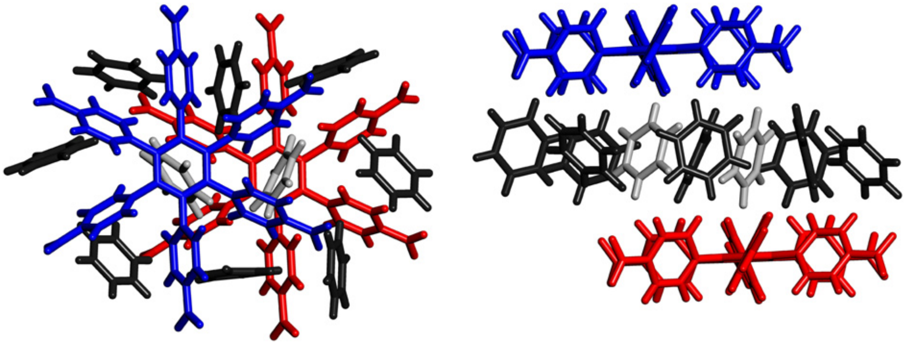


Figure 4. Top view (left) and side view (right) of the alternating monolayers found in crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/benzene, showing two molecules of nitroarene **1** in different layers (blue and red) separated by a layer consisting of molecules of benzene (black and gray). Each molecule in gray directs a C–H bond toward the center of the hexaphenylbenzene core of a neighboring molecule of nitroarene **1**.

type **IV** (Fig. 2), and they can be considered to play a key role in maintaining the integrity of the layer.

In crystals grown from both DMF/benzene and DMF/dioxane, monolayers composed of nitroarene **1** are separated by monolayers of included solvent. Each molecule of included dioxane has six neighbors within the plane, and two molecules of guest are partially accommodated within spaces above and below the central aromatic ring of each molecule of host **1**, creating two C–H···aromatic interactions with H···centroid distances of 2.65(1) Å. Again, no significant intralayer C–H···O interactions of NO_2 groups are present, but each molecule of nitroarene **1** engages in multiple C–H···O interactions with molecules of dioxane in adjacent layers (H···O distances in the range 2.44(1)–2.74(1) Å).

2.2.3. Structure of crystals of hexakis(4-nitrophenyl)benzene (1) grown from DMF/acetonitrile.

Crystals grown by allowing vapors of acetonitrile to diffuse into solutions of

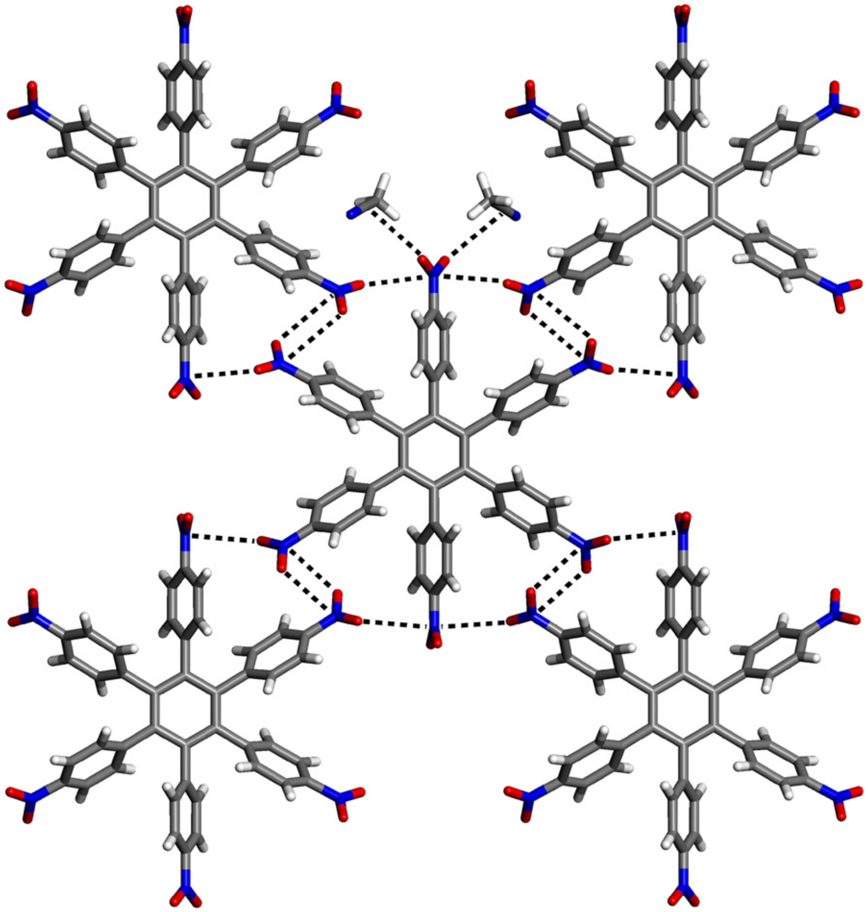


Figure 5. View of the structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/acetonitrile, showing significant N···O interactions (N···O distances <3.5 Å) between NO_2 groups of a central molecule of nitroarene **1** and its four coplanar neighbors, as well as C···O interactions with two included molecules of acetonitrile. All interactions are represented by broken lines. Atoms of hydrogen appear in white, carbon in gray, nitrogen in blue, and oxygen in red.

nitroarene **1** in DMF were found to belong to the monoclinic space group *C*2/*c* and to have the composition **1**·2 acetonitrile, as established crystallographically (Table 1). The ratio of included guests per molecule of host **1** (2:1) is substantially lower than it is in crystals grown from DMF/benzene and DMF/dioxane (7:1), providing immediate evidence of underlying structural differences. Acetonitrile occupies only 18% of the volume of the crystals, and again no DMF is included (Table 2). Molecules of nitroarene **1** lie in well-defined monolayers and adopt a chiral propeller-shaped conformation, with torsional angles between the central and outer rings in the range 60–68° (Table 3). Each layer of nitroarene **1** contains an equal number of the two enantiomers. Unlike the layers in crystals grown from DMF/benzene or DMF/dioxane, which are separated by intervening monolayers of guest, layers of nitroarene **1** in crystals grown from DMF/acetonitrile are in direct contact, and the smaller guests are able to occupy spaces within the layers of host. Again, cohesion within the layers can be attributed to multiple N···O interactions of NO_2 groups, but each molecule of nitroarene **1** is linked to only four neighbors within the same layer (Fig. 5). In addition, each molecule of nitroarene **1** interacts with four neighbors in each of the two adjacent layers by participating in a total 12 significant C–H···O interactions of NO_2 groups, with H···O distances in the range 2.31(1)–2.75(1) Å (Fig. 6a). Most of these interactions (8) involve hydrogen atoms *ortho* to NO_2 groups (motif **II**, Fig. 1), and *meta* hydrogen atoms are engaged in only four interactions (motif **III**, Fig. 1), possibly because the characteristic geometry of the hexaphenylbenzene core of compound **1** makes the *meta* hydrogen atoms less accessible.

In the observed structure, a total of 16 N···O interactions per molecule of nitroarene **1** are shorter than 3.5 Å. No cyclic trimers are observed (motif **VI**, Fig. 2), but eight of the interactions are involved in the formation of cyclic dimers (motif **V**, Fig. 2). N···O distances in the dimeric motifs (3.366(4) and 3.455(3) Å) are longer than those observed in simple motif **IV**, which lie in the range 3.103(3)–3.121(1) Å. This may arise from a combination of dipolar attractions and repulsions in the dimeric motif or from constraints introduced by the inherent difficulty of packing hexaphenylbenzene **1**, which may prevent dimeric motif **V** from attaining its optimal geometry.

Pairs of guest molecules are included within cages bounded by four molecules of nitroarene **1** in the same layer and capped by two other molecules of host in adjacent layers (Figs. 7a and 8a). Interactions of guests with the host include (1) weak N–O···C interactions (O···C distances of 3.171(4) Å) involving an NO_2 group of the host and the CN groups of two guests (Fig. 5); (2) a C–H···O interaction involving an NO_2 group of the host and the CH_3 group of the guest; and (3) various C–H···N interactions involving aryl groups of the host and the CN group of the guest.

2.2.4. Structure of crystals of hexakis(4-nitrophenyl)-benzene (1) grown from DMF/acetone. Crystals grown by allowing vapors of acetone to diffuse into solutions of nitroarene **1** in DMF proved to belong to the monoclinic space group *C*2/*c* and to have the composition **1**·2 acetone, as determined crystallographically (Table 1). The resulting structure is closely similar to that of crystals grown from

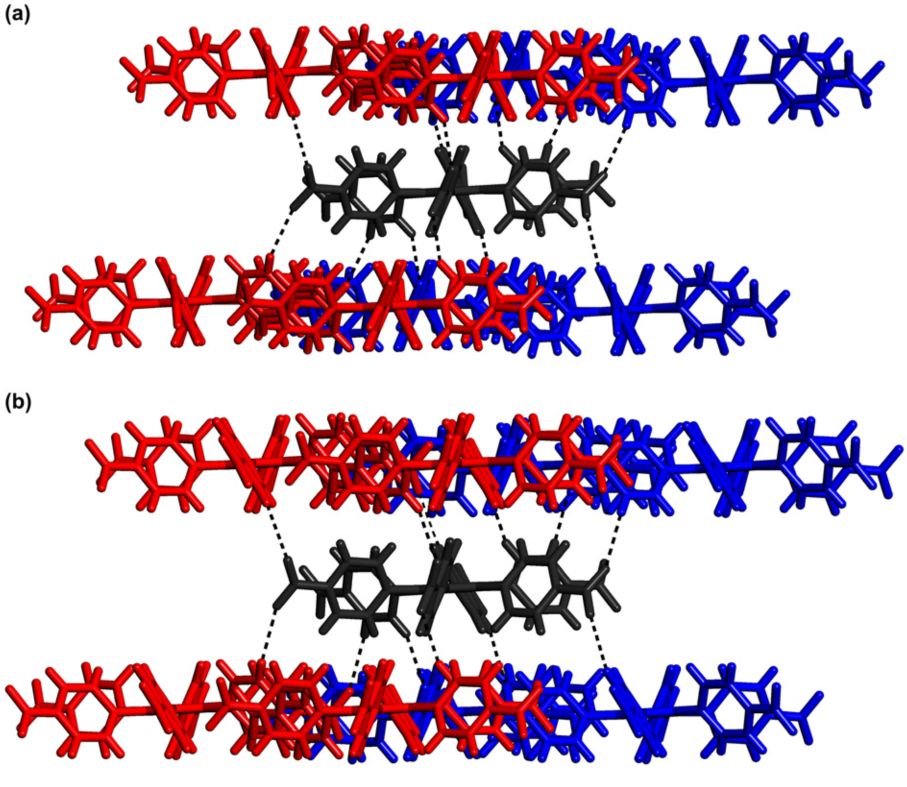


Figure 6. (a) View of the layered structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/acetonitrile, showing significant interlayer C–H···O interactions (H···O distances less than 2.75 Å) of a central molecule of nitroarene **1** (black). The interactions, which are represented by broken lines, involve four molecules of compound **1** (red and blue) in each of the two adjacent layers. (b) Analogous view of the layered structure of crystals of nitroarene **1** grown from DMF/acetone.

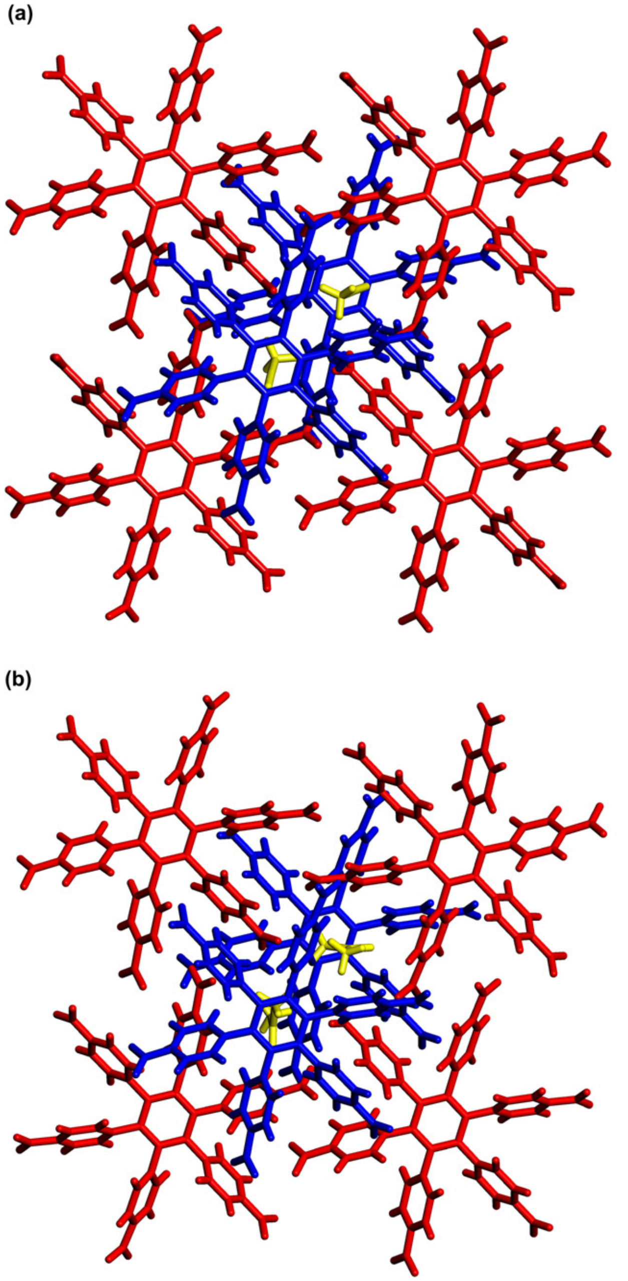


Figure 7. (a) View showing molecules of acetonitrile (yellow) included in crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/acetonitrile. The guests occupy a cage bounded by four coplanar molecules of host **1** (red) and capped by two other molecules of the host in adjacent layers (blue). (b) Similar view showing the cage in which acetone is included in crystals of host **1** grown from DMF/acetone.

DMF/acetonitrile. Included acetone occupies 19% of the volume of the crystals, and again no DMF is included (Table 2). Molecules of nitroarene **1** define layers and assume a characteristic chiral propeller-shaped conformation, with torsional angles between the central and outer rings in the range 62–68° (Table 3). Layers of nitroarene **1** incorporate both enantiomers in a 1:1 ratio, and molecules of acetone are included in pairs within each layer in volumes bounded by four coplanar molecules of host and two others in adjacent layers (Figs. 7b and 8b). Again, the individual layers are maintained by multiple N···O interactions of NO_2 groups. Each molecule of nitroarene **1** is joined to four neighbors within the same layer (see the Supplementary data for figure) by a total of 12 significant N···O interactions (distances less than 3.5 Å). Of these interactions, four are present in cyclic dimers (motif **V**, Fig. 2). N···O distances in the dimeric motifs (3.263(3) Å) are similar to those found in simple motif **IV** (3.271(2)–3.474(2) Å). This supports our suggestion, based on analysis of N···O distances in crystals grown from DMF/acetonitrile, that there is no simple correlation between distance and the number of interactions per NO_2 group. Adjacent layers engage in multiple C–H···O interactions formed by NO_2 groups of the host (Fig. 6b).

The included molecules of acetone interact with the host in several ways. Of particular interest are N···O interactions between the carbonyl oxygen atom of the guests and an NO_2 group of the hosts. In these interactions, the N···O distance is 3.051(3) Å and the C–N···O angle is 77.60(12)°. Only one other structure incorporating an N···O interaction beween a carbonyl donor and an NO_2 acceptor has been reported.[19] In the structure of crystals of nitroarene **1** grown from DMF/acetone, included molecules of acetone also serve as donors in one C–H···O interaction in which an NO_2 group of the host acts as acceptor, with an H···O distance of 2.62(1) Å.

2.2.5. Structure of crystals of hexakis(4-nitrophenyl)benzene (1) grown from DMF/ethanol. Crystals grown by allowing vapors of ethanol to diffuse into solutions of nitroarene **1** in DMF were found to belong to the monoclinic space group $P2_1/n$ and to have the composition $\mathbf{1}\cdot 2$ ethanol, as established crystallographically (Table 1). The resulting structure is closely similar to those of crystals grown from DMF/acetonitrile and DMF/acetone and will be described only briefly. Included ethanol occupies 14% of the volume of the crystals (Table 2). Molecules of nitroarene **1** define layers and adopt an irregular propeller-shaped conformation, with torsional angles in the range 71–80° (Table 3). Layers of nitroarene **1** are composed of both enantiomers in a 1:1 ratio, and paired molecules of ethanol are included within each layer in cages bounded by a total of six molecules of host **1** (Fig. 8c). Again, the individual layers are maintained primarily by multiple N···O interactions of NO_2 groups. Each molecule of nitroarene **1** is linked to four neighbors within the same layer by a total of 12 significant N···O interactions (see the Supplementary data for figure), including four in cyclic dimers (motif **V**, Fig. 2). Adjacent layers engage in multiple C–H···O interactions formed by NO_2 groups of the host and both *ortho* and *meta* hydrogen atoms. Ethanol interacts with the host in the following ways: (1) The OH group of each guest donates a hydrogen bond to the oxygen atom of an NO_2 group (H···O distance of 1.95(1) Å, O–H···O angle of 166(1)°); (2) the CH_2 group interacts with an NO_2 group of the host by serving as the donor in a C–H···O hydrogen bond; and (3) the oxygen atom of each guest engages in an N···O interaction with an NO_2 group (N···O distance of 3.366(4) Å). This demonstrates that the ability of groups other than NO_2 to participate in N···O interactions includes not just carbonyl compounds such as acetone (as observed in the structure of crystals of nitroarene **1** grown from DMF/acetone), but also extends to other classes of molecules with functional groups incorporating oxygen.

2.2.6. Structure of crystals of hexakis(4-nitrophenyl)benzene (1) grown from DMF/nitrobenzene. All the

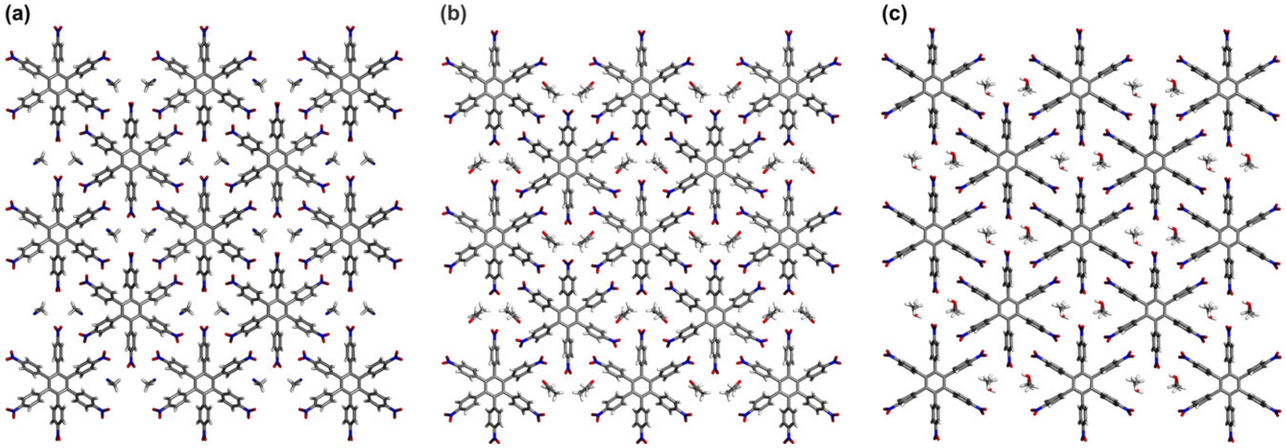


Figure 8. Views of the structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from; DMF/acetonitrile (a), DMF/acetone (b), and DMF/ethanol (c), showing how pairs of guests are included within characteristic layers of host **1** maintained by N···O interactions.

crystals of nitroarene **1** grown from solutions in DMF containing benzene, dioxane, acetonitrile, acetone, and ethanol have structures that fall into two closely related categories. In crystals of type I (obtained from DMF/benzene and DMF/dioxane), molecules of host **1** form relatively well-packed layers separated by intervening layers of guests, which are a major component of the crystal. Crystals of type II are composed exclusively of layers in which smaller quantities of guests occupy spaces between molecules of host **1**, which are less tightly packed than in crystals of type I. Surprisingly, no DMF is included in crystals grown under any of these conditions. This suggests that DMF is not readily accommodated by either of the two observed structural types.

Further experimentation showed that crystals grown by exposing solutions of nitroarene **1** in DMF to vapors of nitrobenzene belong to the monoclinic space group $P2_1$ and have the composition **1**·2 DMF, as established crystallographically (Table 1). As suggested by the failure of crystals of types I and II to accommodate DMF, host molecules in crystals of inclusion compound **1**·2 DMF are arranged in a distinctly different way (Figs. 9 and 10). Layers maintained by multiple N···O interactions of NO_2 groups are again present, but they are now corrugated, and the least-squares planes of adjacent molecules of host **1** form an angle of 51° (Fig. 9). As shown in Figure 10, each molecule of host **1** is linked to four neighbors in the same corrugated layer by a total of twelve significant N···O interactions (distances less than 3.5 Å). Of these interactions, four are incorporated in cyclic dimers (motif **V**, Fig. 2). Adjacent corrugated layers engage in multiple C–H···O interactions involving NO_2 groups of the host.

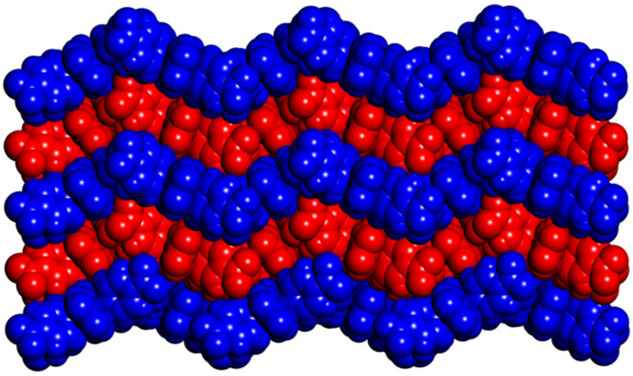


Figure 9. View of the structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/nitrobenzene, showing adjacent corrugated layers in red and blue.

In crystals grown from DMF/nitrobenzene, molecules of nitroarene **1** adopt a propeller-shaped conformation, with torsional angles between the central and outer rings in the range 73–89° (Table 3). In DMF/benzene, DMF/acetonitrile, DMF/acetone, and DMF/ethanol, host **1** forms racemic crystals composed of both enantiomers. In contrast, crystals grown from DMF/nitrobenzene are conglomerates, each consisting of a single enantiomer. Included DMF occupies 22% of the volume of the crystals (Table 2), and the guests are paired within cages bounded by six molecules of host **1**. The principal interactions between guest and host are C–H···O hydrogen bonds in which the oxygen atom of DMF serves as an acceptor and the CH_3 groups as donors.

3. Conclusions

The behavior of hexakis(4-nitrophenyl)benzene (**1**) confirms that intermolecular N···O interactions of NO_2 groups can help crystal engineers position molecules with a useful degree of predictability, particularly when stronger interactions such as hydrogen bonds are absent, and when competition with other weak interactions is limited. Derivatives of hexaphenylbenzene typically crystallize as layered structures in which significant quantities of guests are included in spaces between the layers or within them. In the case of nitroarene **1**, this tendency is visibly reinforced by multiple intermolecular N···O interactions of NO_2 groups within the layers, which help to hold the layers together and determine how their molecular constituents are positioned. As a result, nitroarene **1** crystallizes to give six pseudopolymorphs with closely related structures. In contrast, recent studies have established that hexakis(4-cyanophenyl)benzene (**2**), a similar molecule unable to engage in N···O interactions, crystallizes as eight pseudopolymorphs with few

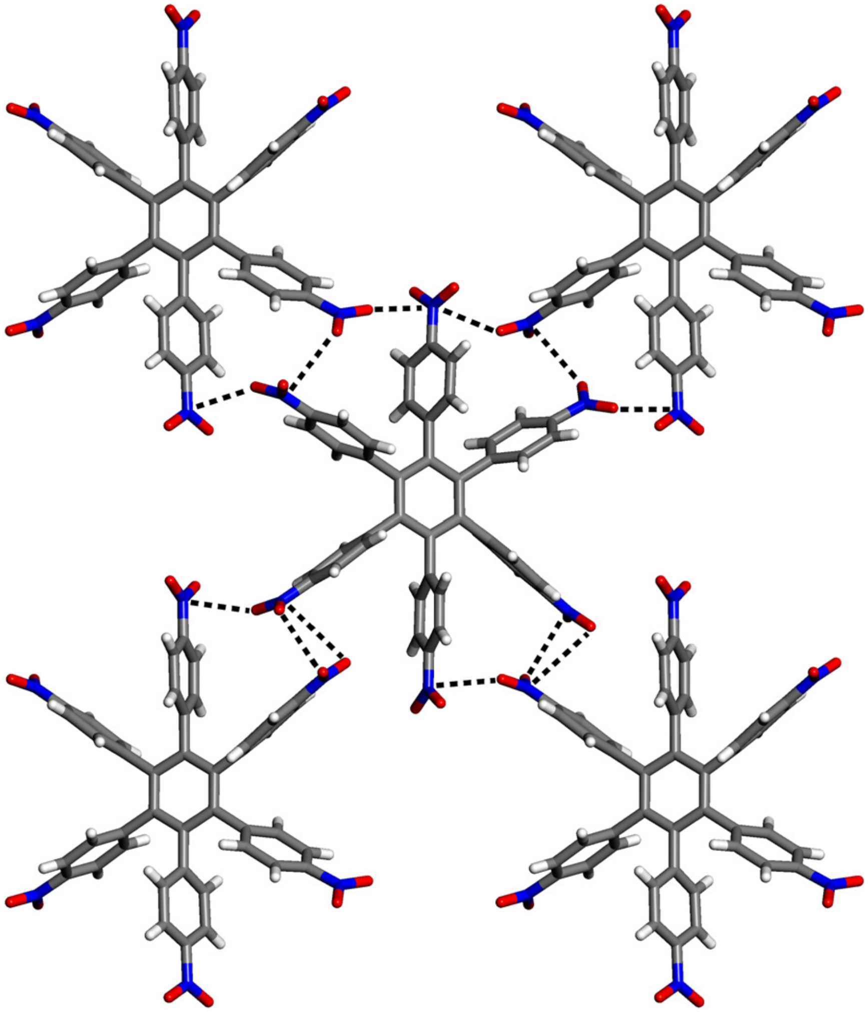


Figure 10. View of the structure of crystals of hexakis(4-nitrophenyl)benzene (**1**) grown from DMF/nitrobenzene, showing significant N···O interactions (N···O distances <3.5 Å) between NO_2 groups of a central molecule of nitroarene **1** and its four coplanar neighbors. The interactions are represented by broken lines. Atoms of hydrogen appear in white, carbon in gray, nitrogen in blue, and oxygen in red.

shared structural features.[25,26] The different behavior of compounds **1** and **2** underscores the potential of intermolecular N···O interactions of NO_2 groups in crystal engineering.

4. Experimental

4.1. Synthesis of hexakis(4-nitrophenyl)benzene (1)

During 5 min, solid hexaphenylbenzene (1.75 g, 3.27 mmol)[28] was added in small portions to a stirred mixture of fuming HNO_3 (40 mL) and concentrated H_2SO_4 (20 drops) kept at 0 °C. At the end of the addition, a mixture of CH_3COOH (8 mL) and $CH_3COOC_2H_5$ (4 mL) was added dropwise. The cooling bath was removed, and then the mixture was stirred for 20 h and poured into cold H_2O (150 mL). The resulting precipitate was collected by filtration, washed with acetone, dried, and then crystallized from DMSO. The crystals were isolated by filtration and washed with acetone to give hexakis(4-nitrophenyl)benzene (**1**; 1.57 g, 1.95 mmol, 60%) as a colorless solid. A sample of analytical purity was obtained by recrystallization from DMF: mp>360 °C (lit.[27] 440–450 °C (dec)); IR (KBr) 1602, 1530, 1350, 860 cm^{-1}; ^1H NMR (400 MHz, DMF-d_7) δ 7.44 (d, ^3J=8.5 Hz, 12H), 7.92 (d, ^3J=8.5 Hz, 12H); ^{13}C NMR (75 MHz, DMF-d_7) δ 123.7, 133.7, 140.1, 146.8, 147.4.

4.2. X-ray crystallographic studies

Structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.[31] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to aromatic rings were placed in ideal positions and refined as riding atoms. The structures have been deposited at the Cambridge Crystallographic Data Centre and assigned the deposition numbers CCDC 634938–634943.

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Supplementary data

Additional crystallographic details, including ORTEP drawings and tables of structural data for pseudopolymorphs of hexakis(4-nitrophenyl)benzene (**1**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.101.

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