

Removal of Conflicting Molecular Symmetries Restores a Hexagonal Array of Six-Fold Phenyl Embraces in a bis(Triptyl)-Containing Compound. I. Crystals of 1,1,1,6,6,6-Hexaphenyl-2,4-hexadiyne

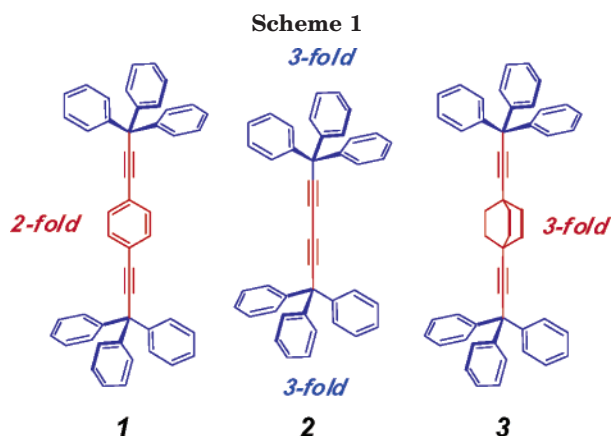
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Received March 19, 2004

ABSTRACT: Previously reported structures of 1,4-bis(3,3,3-triphenylpropynyl)benzene (**1**) showed molecules adopting a C_i point group in the triclinic space group $P\bar{1}$. Reasoning that a symmetry conflict between the 3-fold symmetric triphenylmethyl groups and the 2-fold symmetric phenyl group may be responsible for the low symmetry crystal structure, it was speculated that the removal of the central benzene ring might lead to crystal symmetries where the molecular 3-fold axes might be elicited. To test that, we analyzed the crystallization and packing of 1,1,1,6,6,6-hexaphenyl-2,4-hexadiyne (**2**). Satisfyingly, compound **2** was found to crystallize in the rhombohedral space group $R\bar{3}$ with three different molecular structures, one displaying a chiral C_3 point group and the others a meso conformation with an S_6 point group.

In efforts to engineer molecular motions in crystalline solids for potential materials application,¹ we have recently investigated various compounds with a tendency to adopt packing arrangements that permit the rotation of a central group. Several structures consisting of triptyl² or triptycyl³ groups attached to 1,4-diethynylphenylenes have been analyzed, and some of their crystals have been found to display 2-fold phenylene rotation with rate constants as high as 10^8 Hz at room temperature.¹ Having a frame that is held rigidly in the crystal lattice (shown in blue) and a central group that experiences rotary motion (in red), we refer to those structures as “molecular gyroscopes”. 1,4-Bis(2-triptyethynyl)benzene (**1**) (Scheme 1) is the simplest example in the triptyl series.



Knowing that physical properties and materials science applications depend on crystal symmetry,⁴ it would be desirable to understand the influence of molecular structure on the formation of certain crystal systems. Fortunately, certain aspects of the packing structures of compounds with triphenylmethyl groups such as **1** are relatively well-understood thanks to the extensive work of Dance and co-workers.⁵ An interaction described as a 6-fold phenyl embrace, or 6PE (Figure 1), has been identified as a remarkably robust supramolecular synthon with a great potential in crystal engineering.⁶ The 6PE occurs as a result of complementary edge-to-face interactions between adja-

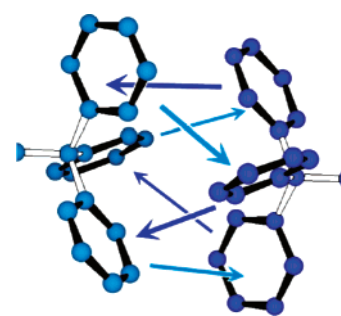


Figure 1. Schematic representation of the 6PE. The light blue arrows indicate the interaction between the edge of a light blue ring with the face of a dark blue ring. Complementary interactions involving the edge of the blue rings are shown with arrows in dark blue (from ref 5a).

cent Ph_3X groups (XPh_3 - - Ph_3X). A frequent occurrence of 6-fold embraces with exact $\bar{3}$ symmetry aligned with the trigonal axes of hexagonal or rhombohedral lattices and its “potency” were noted, as many examples were found where solvent molecules and associated components (e.g., counterions) crystallized with enforced disorder at 3-fold symmetry sites.⁵

In our work with **1** and related compounds,² we have consistently observed the 6PE motif.⁷ However, an obvious conflict arises when the 3-fold symmetry of the triptyl groups in **1** is combined with the 2-fold symmetry of the central phenylene so that crystals are formed in the triclinic space group $P\bar{1}$. Given that the phenyl group seems unwilling to disorder over a 3-fold symmetry site, it was of interest to investigate whether 1,1,1,6,6,6-hexaphenyl-2,4-hexadiyne (**2**), lacking the central 2-fold rotor, or 1,4-bis(3,3,3-triphenylpropynyl)bicyclo[2.2.2]octane (**3**), with a rotor of matching symmetry, might lead to crystal systems and space groups of higher symmetry.

A literature search revealed that Hart et al. had reported a series of clathrates formed with several substituted 1,3-butadiynes, which included a chloroform clathrate of **2**.⁸ Compound **3** has never been reported, and its synthesis is now in progress in our group. Given that no crystal structure was provided for **2**, we decided to carry out a detailed investigation. Out of four possible point group symmetries for each triptyl group (C_1 , C_3 , C_{3v} , and C_s), those shaped as a propeller (C_1 , C_3) are significantly more likely.⁹ Molecular point groups with the latter are C_1 , C_2 , and C_3 ,

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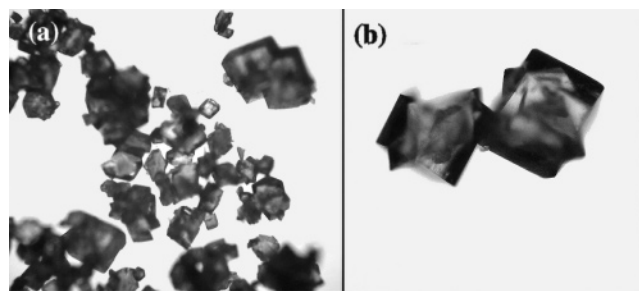


Figure 2. (a) Micrograph of crystals of **2** through cross-polarizers showing the typical block morphology and (b) a close up of interpenetration twins.

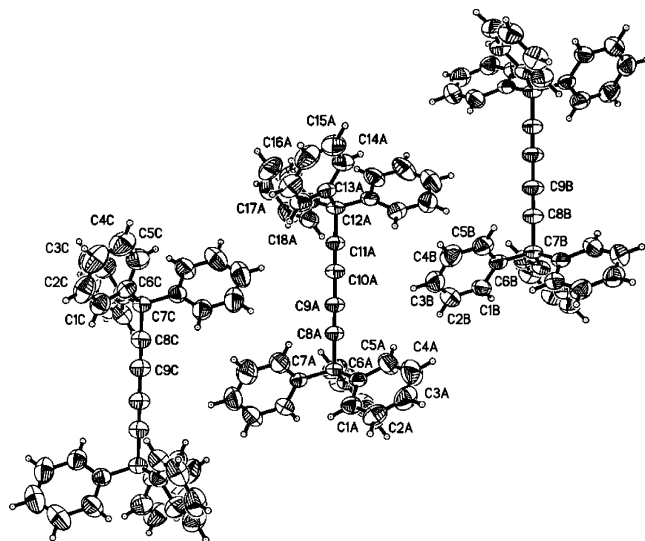


Figure 3. Three molecules of compound **2**, A (center), B (left), and C (right), with their unique atomic positions labeled. The displacement ellipsoids are shown at the 50% probability level, and the H atoms are shown as spheres of arbitrary size. The compound packs with the trityl groups embracing and the long axis of the molecules in a parallel arrangement (on the right).

with homochiral propellers, and C_i , C_s , and S_6 , with propellers of opposite chirality.

We had previously obtained compound **2** in our lab as a small impurity during the synthesis of **1** by Sonogashira coupling between 1,4-diiodobenzene and 3,3,3-triphenylpropyne.² Larger samples were prepared by standard Glaser coupling of 3,3,3-triphenylpropyne in the presence of copper(I) chloride and oxygen.¹⁰ Knowing that a CHCl_3 clathrate of **2** had been reported, we investigated its crystallization from a variety of pure solvents by slow evaporation. Remarkably, crystals of **2** were only obtained in a solvent-free form from CH_2Cl_2 , benzene, toluene, *para*-difluorobenzene, and 2,6-dimethylnitrobenzene. The choice of solvents was strongly influenced by its low solubility in other conventional solvents. Highly symmetric, colorless, regular cubes, of ca. 0.1–2 mm per side had a strong tendency to form interpenetrated twins under all of the crystallization conditions explored (Figure 2). Identical unit cell parameters were determined for all of those crystals, and a full structure determination was carried out with a regular cube, nontwinned specimen grown from dichloromethane.

To our satisfaction, the structure of **2** was solved from diffraction data collected at 298 K in a rhombohedral crystal system in the space group $R\bar{3}$ with 12 molecules per unit cell.^{11,12} The asymmetric unit is composed of three fractional molecules labeled A, B, and C (Figure 3).¹³ With

Table 1. Torsion Angles Presented by the Phenyl Groups in Molecules A–C

molecule	atoms involved		angle ($^\circ$)
	$\text{C}_{\text{alkyne}}-\text{C}_{\text{alkane}}-\text{C}_{\text{ipso}}-\text{C}_{\text{ortho}}$		
A	$\text{C}_{1\text{A}}-\text{C}_{6\text{A}}-\text{C}_{7\text{A}}-\text{C}_{8\text{A}}$		140.10(11)
	$\text{C}_{11\text{A}}-\text{C}_{12\text{A}}-\text{C}_{13\text{A}}-\text{C}_{14\text{A}}$		138.63(13)
B	$\text{C}_{1\text{B}}-\text{C}_{6\text{B}}-\text{C}_{7\text{B}}-\text{C}_{8\text{B}}$		131.73(12)
C	$\text{C}_{5\text{C}}-\text{C}_{6\text{C}}-\text{C}_{7\text{C}}-\text{C}_{8\text{C}}$		147.14(14)

Table 2. Close Contacts in the Crystal Structure of **2**

molecule	atoms involved	distance (\AA)
A	$\text{C}_{1\text{A}}-\text{H}_{4\text{A}}$	2.845
	$\text{C}_{2\text{A}}-\text{H}_{4\text{A}}$	2.866
	$\text{C}_{2\text{A}}-\text{H}_{1\text{B}}$	2.900
B	$\text{H}_{1\text{B}}-\text{C}_{2\text{A}}$	2.900
C	no close contacts	

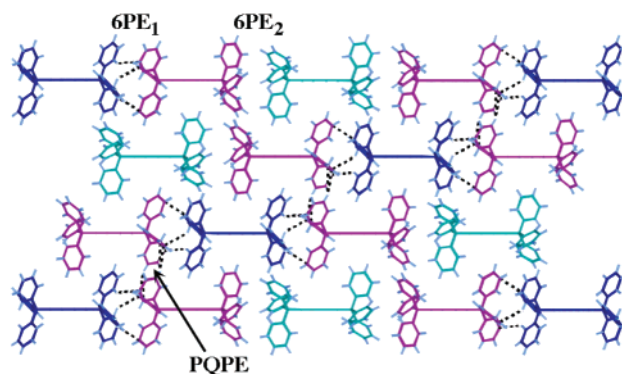


Figure 4. View of the (1,1,0) plane with the c -axis in the horizontal direction showing two types of 6PEs (6PE_1 and 6PE_2) between molecules A (violet) and B (dark blue) and between molecules A and C (teal). The 6PE embrace between molecules A and B is characterized by close contacts depicted with dashed lines. PQPEs also occur between molecules in neighboring columns (A–A' and B–C).

its two trityl groups adopting homochiral propeller conformations, molecule A has its long molecular axis along the crystallographic C_3 axis of symmetry. It should be pointed out that as required by the space group symmetry, both enantiomers, A and A', are present in the crystal. Molecules B and C have *meso* structures, with coincident molecular and crystallographic $\bar{3}$ (S_6) axes. As the two trityl groups in molecule A possess slightly different conformations, its structure is described by the atomic positions of one phenyl ring from each trityl group and the four carbon atoms along the dialkyne-containing chain. The structures of molecules B and C are described by one phenyl ring, the methane carbon, and one acetylene fragment. The dihedral angles between the planes of the phenyl rings and the vector given by the axis of the dialkyne are listed in Table 1. These angles have a 16° range, from 131.73° for molecule B to 147.14° for molecule C.

Compound **2** packs in columns along the c -direction in a BACA' repeating pattern with A and A' representing molecules of opposite chirality. Close contacts are listed in Table 2 and are illustrated by dotted lines in Figure 4. Two types of 6PEs can be distinguished along these columns. The first one, labeled 6PE_1 in Figure 4, is characterized by three close contacts between trityl groups of molecule B and one of the trityl groups of molecule A. The distance between the tetrahedral carbons of the interacting trityl groups is 6.145 \AA . The second one (6PE_2) occurs between the other trityl group of molecule A and the trityl groups of molecule C; it has no close contacts, and the distance between the trityl groups tetrahedral carbons is 6.942 \AA . Further analysis of the packing structure reveals a series

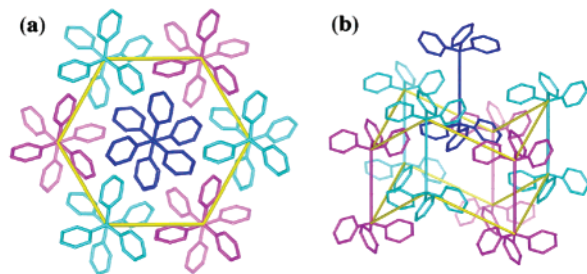


Figure 5. (a) Three-fold view of the crystal structure looking down the *c*-axis showing a projection of molecules involved in a HA6PE highlighted in yellow and (b) view of the HA6PE with the *c*-axis vertical showing the chairlike arrangement of trityl groups.

of offset face-to-face, vertex-to-face, and edge-to-face interaction between molecules of adjacent columns. This side-by-side arrangement has been referred to as a parallel quadruple phenyl embrace (PQPE).⁵

A view down the *c*-axis in Figure 5a shows the 3-fold symmetry of **2** and how the three crystallographically different molecules A, B, and C adopt a hexagonal array of 6PEs (HA6PE).⁵ When the HA6PE is viewed from the side (Figure 5b), the 6PEs that define the hexagon are positioned with their vertexes falling in a chairlike arrangement.

In conclusion, removal of the central phenylene in compound **1** to give hexadiyne **2** conforms to the symmetry expectations regarding the packing of trityl compounds outlined by Dance et al. Given that rhombohedral crystals have their only optic axis along their $\bar{3}$ direction, a similar packing structure in the case of compound **3** could have a favorable influence on its electrooptic properties. We speculate that analogues of **3** with polar substituents on the bicyclo[2.2.2]octane 3-fold rotor may have electrooptic properties addressable with external electric fields.¹⁴ Studies are in progress to evaluate this possibility, and results with compound **3** will be reported in due course.

Acknowledgment. This work was supported by the National Science Foundation through Grants DMR0307028 and CHE9871332 (X-ray diffractometer).

Supporting Information Available: Crystallographic information (CIF) file for compound **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Selected crystal data for compound **2**: C₄₂H₃₀, colorless blocks, MW = 534.66, rhombohedral, space group $R\bar{3}$, $a = b = 13.9822(5)$ Å, $c = 53.094(4)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $Z = 12$, $\rho_{\text{calcd}} = 1.185$ mg/m³, $F(000) = 3384$, $\lambda = 0.71073$ Å, $\mu(\text{Mo K}\alpha) = 0.172$ mm⁻¹, $T = 298(2)$ K, crystal size = $0.40 \times 0.40 \times 0.40$ mm³. Of the 19131 reflections collected ($1.72^\circ \leq \theta \leq 28.30^\circ$), 4897 [$R(\text{int}) = 0.0318$] were independent reflections; max/min residual electron density 183 and -136 e nm³, $R1 = 0.0477$ [$I > 2\sigma(I)$], and $wR2 = 0.1418$ (all data).
- (12) Aside from differences in unit cell dimensions and bond distances, the crystal structure of **2** is isomorphous with that of bis(triphenylsilicon)carbodiimide. Please see Sheldrick, G. M.; Taylor, R. *J. Organomet. Chem.* **1975**, *101*, 19–25.
- (13) The occurrence of more than one conformer within a given crystal structure is referred to as conformational polymorphism. Bernstein, J. In *Solid State Organic Chemistry*; Desiraju, G., Ed.; Elsevier: Amsterdam, 1987; pp 471–518.
- (14) While crystals analyzed with polarized light along the optic axis are isotropic, the alignment of otherwise disordered dipoles within the internal rotor of **3** is expected to produce birefringence.

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