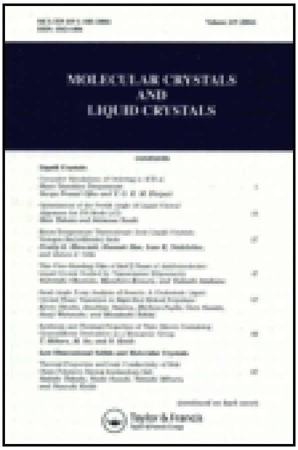

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Crystalline Molecular Gyroscopes: The Effects of Subtle Molecular Differences on the Crystal Packing of Triphenylmethyl and Triphenylsilyl Stators

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Single crystals of molecular gyroscopes, 1,4-bis(3,3,3-triphenylpropynyl)benzene and 1,4-bis(triphenyl-silanylethynyl)-benzene were studied by single crystal X-ray diffraction (XRD) analysis and their packing tendencies were compared to those of analogous structures without the central phenylene rotator.

Keywords: crystal engineering; molecular gyroscopes; six-fold phenyl embrace; X-ray diffraction

INTRODUCTION

Packing forces in molecular crystals are determined by a large number of weak, attractive and repulsive, equilibrating interactions, including π-π stacking, dipole-dipole and van der Waals interactions. The strength of these interactions depends on their nature, the composition of the groups involved, and the distances and geometries over which they occur. In general, there is an inverse relationship between the distance and strength of the interaction, which may be given as a function of $1/r^x$, where r is the distance between the atoms involved, with x varying from 2 for Coulombic interactions, up to 6 and 12 for van der Waals forces [1]. With such strong distance dependence, it is

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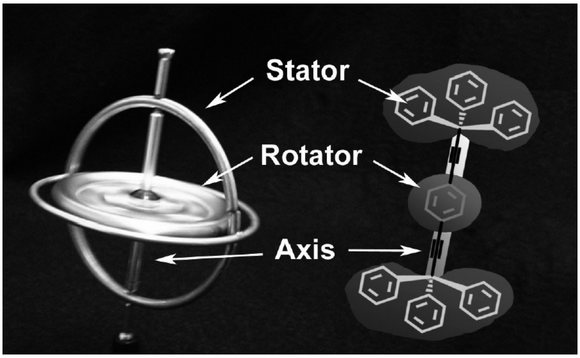


FIGURE 1 Toy gyroscopes have a rigid outer frame encasing a mass, which rotates around an ideally frictionless axis. Molecular analogs of gyroscopes should possess the same three components.

not surprising that any small change in molecular structure has the potential of creating considerable changes in the molecular packing. The purpose of this paper is to investigate how a very small change in the structure of a molecular gyroscope may affects its crystal packing.

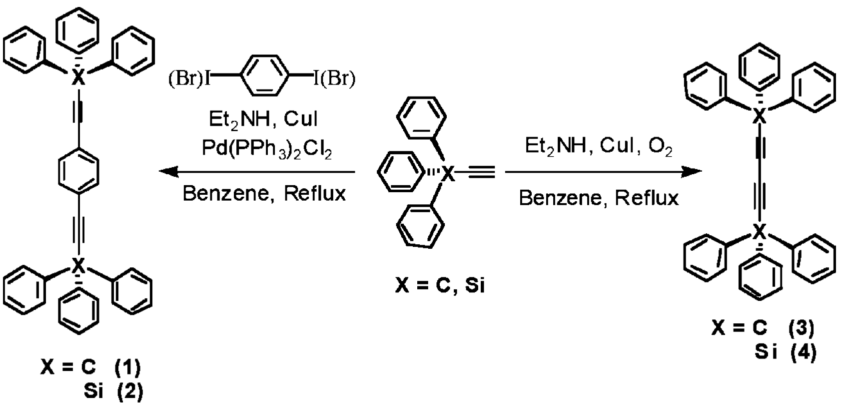
Macroscopic toy gyroscopes have a rigid outer frame (stator) encasing a mass (rotator), which rotates around an ideally frictionless axle (Fig. 1). Molecular analogs to toy gyroscopes should possess the same three components: a stator, a rotator, and an axle [2]. Through molecular engineering, we have designed a family of molecular gyroscopes that exhibit rapid 180° phenylene rotation (flipping) in the solid state [3]. The simplest of these molecules (molecular gyroscopes **1**) consists of a *bis*-triphenylmethyl (trityl) stator, a dialkynyl axle, and a *para*-phenylene rotator (Fig. 1). At room temperature, the phenylene of **1** exhibits 180° flipping motions with an average correlation time of 0.9 ms ($\sim$1100 flips per second) and a barrier to rotation of 11.6 kcal/mol [4]. To determine the effects of a minor perturbation on the structure, in this paper we will compare the crystal packing of molecular gyroscope **1** to that of an analogous molecular gyroscope **2**, which has a *bis*-triphenylsilyl stator in place of the triphenylmethyl stator in **1** (Scheme 1). The suggested substitution should create small changes in the structure. In addition to the obvious replacement of carbon by silicon, the bond lengths between the sp^3 hybridized atom and the four substituents should be around 0.4 Å longer for the silane [5]. Due to the larger size of the silicon atom and the longer bond length, the three phenyls are expected to extend farther apart from the center of the molecule. This expansion should result in lower steric crowding and increased flexibility of the three aromatic groups attached to the silane center. These small differences have the potential of dramatically changing the packing structure and dynamic properties of molecular gyroscope **2** as compared to those of molecular gyroscope **1**.

EXPERIMENTAL

Molecular gyroscope **1** can be made by Sonogashira coupling of 3,3,3-triphenylpropyne and diiodobenzene (Scheme 1) [4]. In the presence of oxygen, this reaction will also lead to the dimerization of the terminal alkyne forming 1,1,1,6,6,6-hexaphenyl-2,4-hexadiyne, **3** (Scheme 1). Large amounts of pure diyne **3** can be prepared using standard Glaser coupling of 3,3,3-triphenylpropyne in the presence of copper (I) chloride and oxygen [6].

Molecular gyroscope **2** and *bis*-(triphenylsilanyl)-1,4-butadiyne (**4**) can be prepared by substituting triphenylsilylacetylene for the 3,3,3-triphenylpropyne in the reaction used to prepare **1** and **3**, respectively. Compounds **2** and **4** were noticeably more soluble than the carbon analogs **1** and **3** in common organic solvents, such as dichloromethane, acetone, benzene, toluene, and chloroform.

Single crystal X-ray diffraction analysis of compounds **1**, **2**, and **3** were performed on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (l = 0.71073 Å) operated at 2250 watts power. The detector was placed at a distance of 4.986 cm from the crystal. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The structure was refined using the Bruker SHELXTL (Version 6.12) Software Package.



SCHEME 1

RESULTS AND DISCUSSION

Crystal Structure Analysis

As it was recently reported, the alkynyl dimer (**3**) crystallizes from many different solvents (dichloromethane, chloroform, acetone, benzene, toluene, *para*-diflourobenzene, and 2,6-dimethylnitrobenzene) in a solvent-free structure [7]. The structure was solved in a Rhombohedral crystal system in the space group R-3. There are 12 molecules per unit cell, of which three are unique (A, B, C) (Figure 2). With axially chiral triphenylmethyl groups, molecules A and C are meso and molecule B occurs in D, L forms. The packing structure is characterized by head-to-tail chains along the *c*-axis in the repeat pattern ACA'B, with A and A' representing molecules of opposite chirality. These chains come together to form a close packed hexagonal array in which six chains surround a seventh chain.

The trityl groups are arranged in what is known as a six-fold phenyl embrace (6PE) [8]. The 6PE is characterized by a cyclic arrangement of complementary edge-to-face interaction between adjacent Ph_3X groups (XPh_3----Ph_3X). In this structure, the distance over which the trityl embrace occurs is very different for molecules A and B (6.15 Å), as compared to that for molecules A and C (6.94 Å). This distances are measured from the methane carbon of one trityl group to the methane carbon of the other one (Table 1). The difference between the two 6PE's can also be seen by the presence of short (less than the sum of van der Waals radii) contacts between the phenyl rings of molecules A and B, while there are no close contacts between molecules A and C. The three molecules A, B, and C have a distance between the two methane carbons that is 6.735(15) Å long.

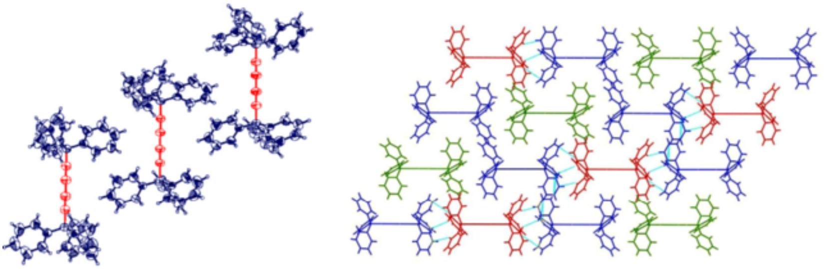


FIGURE 2 Left: Ortep diagram of the trityl dimer, showing the three unique molecules. Right: packing diagram with the three unique molecules in a repeat pattern of ACA'B.

TABLE 1 Length of the Phenyl Embrace in Molecules **1–4**, as Measured from the Central X Nuclei of the Two Ph_3X Groups, where X = C or Si

Molecules	Distance (Å)-XPh_3—Ph_3X-
1–1	7.56
2	6.46
3A–**3**B	6.15
3A–**3**C	6.94
4A–**4**B	6.83
4A–**4**C	6.29
4B–**4**B	6.88
4C–**4**D	6.05
4(1)–**4**(2)	6.44
4(2)–**4**(3)	6.95
4(3)–**4**(3)	5.84

The triphenylsilylacetylene dimer **4** crystallizes in two polymorphs, one polymorph occurs in the rhombohedral crystal system in the space group R-3 and the other in the triclinic crystal system and the space group P-1 (Figure 3) [9]. The molecules in the R-3 structure are packed in a very similar arrangement as that previously seen in the crystal structure of compound **3**. In the unit cell of the R-3 structure of **4** there are 21 molecules, four of which are unique (A, B, C, D). The repeat pattern of the four unique molecules is ABB'A'CDC', where A', B', and C' are of the opposite chirality of molecules A, B, and C. The 'trityl' embrace distances present in this structure range from 6.05–6.88 Å, which are similar to those seen for compound **3**. The Si—Si distances are 7.45(2) Å long, which is 0.75 Å longer than those of compound **3**, as expected for the longer C-Si bonds.

The P-1 structure of the triphenylsilyl acetylene dimer **4** is very similar to the higher symmetry R-3 structures, with the head-to-tail alignment of the molecules, the presence of the 'trityl' embrace, and several unique molecules per asymmetric unit. In this structure there are five molecules in the unit cell, three of which are unique (1, 2, 3). The repeat pattern of the three unique molecules is 1233'2, where 3' is the opposite chirality of molecule 3. The 'trityl' embraces are slightly offset resulting is a subtle tilt of each molecular with respect to the long head-to-tail chain. The trityl embraces are 5.84–6.95 Å long, and the molecules are 7.47(1) Å long.

Molecular gyroscope **1**, with a triphenylmethyl stator and phenylene rotator forms a solvent-free crystal structure from acetone, chloroform, dichloromethane, and diethyl ether. This structure is in a

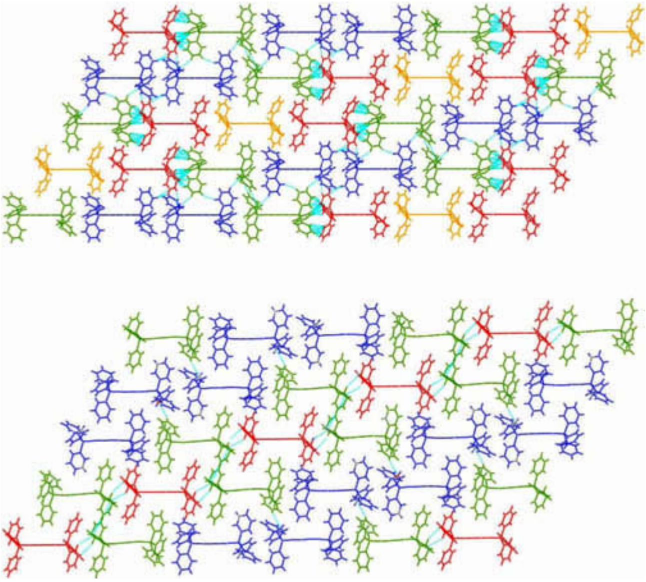


FIGURE 3 Top: Packing diagram of the triphenylsilyl dimer (**3**) in space group R-3 with the four unique molecules in the repeat pattern of ABB'A'CDC'. Bottom: Packing diagram of the second polymorph of **3** in the space group P-1 with the three unique molecules in the repeat pattern 1233'2'.

triclinic crystal system with the space group P-1 (Figure 4). Molecular gyroscope **1** also crystallizes as a clathrate from several aromatic solvents such as benzene, fluorobenzene, and pyridine. It also forms a clathrate with chloroform at −78℃. The unit cell of the solvent free crystal contains one molecule, and half of it represents the asymmetric unit as the molecule sits in an inversion center, which makes the two

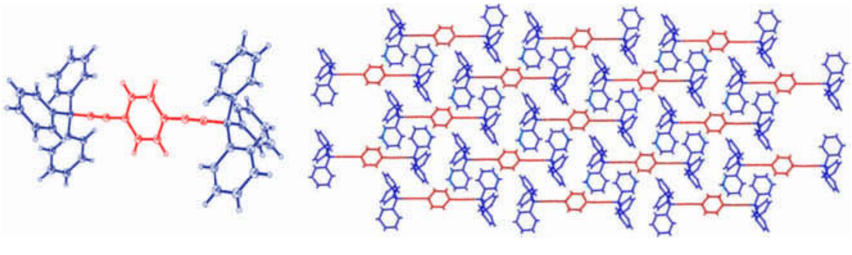


FIGURE 4 Left: Ortep diagram of the trityl phenylene rotor. Right: Packing diagrams looking at the side of the phenylene rotator and at the top of the rotator.

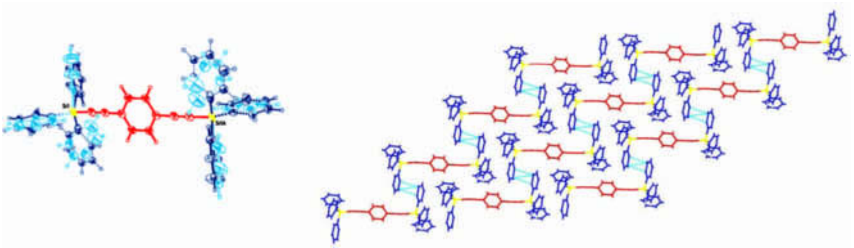


FIGURE 5 Left: Ortep diagram of the triphenylsilanyl phenylene rotor. Note the disorder in all three phenyl rings of the end groups. Right: packing diagrams looking at the side of the phenylene rotator and at the top of the rotator, only one orientation of each phenyl ring is shown for clarity.

chiral trityl groups enantiomeric. The packing of the molecules **1** is very similar to that of the P-1 structure of compound **4**. Long chains of molecular gyroscopes aligned in a head-to-tail manner with slightly offset molecular axes, and a long phenyl embrace distance of 7.56 Å (Fig. 2, Table 1). Interdigitation of phenyl rings of adjacent molecules between the trityl groups form a pocket around the phenylene rotator, which allow for the flipping of the phenylene ring to occur with an energy barrier of ca. 11–14 kcal/mol [4].

Molecular gyroscope **2**, with a triphenylsilyl stator and a phenylene rotator, has similar crystallization characteristics as **1**. Compound **2** forms a solvent free structure from dichloromethane, chloroform, and acetone and it forms a solvent clathrate with benzene. The solvent free structure occurs in the triclinic crystal system in the space group P-1 (Figure 5) [10]. There is one molecule per unit cell and half of it accounts for the crystal asymmetric unit. As with compound **1**, the molecule sits on an inversion center making the two trityl groups enantiomeric. One notable change is the disorder in the phenyl rings. In fact, this is the first structure in this family of compounds to show disorder in the stator. Despite this disorder, the two trityl groups experience a phenyl embrace. However, with their long molecular axis offset in the lattice, the embrace is not a perfect 6PE. The phenyl embrace distance in the structure is 6.46 Å, and Si—Si distance is 11.73 Å.

DISCUSSION

The substitution of a silicon atom for the methane carbon in elongates the structure of **1** and **3** by *ca.* 0.7 Å (Table 2). The geometry around

TABLE 2 Distance Between the two X Nuclei in $Ph_3XCC(C_6H_4)_nCCXPh_3$, where n = 1 for Compounds **1** and **2**, n = 0 for Compounds **3** and **4**

Molecule	Molecular Length (Å)
1	11.02
2	11.73
3A	6.75
3B	6.72
3C	6.72
4A	7.43
4B	7.45
4C	7.47
4D	7.43
4(1)	7.48
4(2)	7.46
4(3)	7.46

the sp^3 hybridized X nucleus in the Ph_3X-CC groups for all molecules **1–4** is slightly flattened from the standard tetrahedral geometry (109.5°). This may be seen by an average value of 107.8–108.1° for the C-(alkyne)-C(methane)-C(ipso) bond angle in the structures of the four compounds (Table 3). Notably, this bond angle has much more variability in the two triphenylsilyl compounds **2** and **4** than in their trityl counterparts (**1** and **3**). The increased variability is also apparent in the torsion angles describing the orientation of the aromatic rings in the trityl groups of the two compounds (Table 3).

The substitution of the methane carbon in compounds **1** and **3** with a silicon atom to form compounds **2** and **4** changes the molecular length, provides increased variability in the bond angles, and improves the solubility in many common organic solvents. Yet, the

TABLE 3 Selected Bond Angles (CXC_{ipso}) and Torsion Angles ($CXC_{ipso}C_{ortho}$) for Molecules **1–4**, where X = C or Si

Molecule (Space Group)	Bond Angle (°) Atoms Involved: CXC_{ipso}		Torsion Angle (°) Atoms Involved: CXC_{ipso} C_{ortho}	
1 (P-1)	CCC_{ipso}	106.5–110.0	$\mathbf{CCC_{\mathit{ipso}}C_{\mathit{ortho}}}$	122.8–161.5
2 (P-1)	$CSiC_{ipso}$	101.8–110.5	$\mathbf{CSiC_{\mathit{ipso}}C_{\mathit{ortho}}}$	109.1–179.7
3 (R-3)	CCC_{ipso}	107.7–108.5	$\mathbf{CCC_{\mathit{ipso}}C_{\mathit{ortho}}}$	131.7–147.1
4 (R-3)	$CSiC_{ipso}$	106.5–109.7	$\mathbf{CSiC_{\mathit{ipso}}C_{\mathit{ortho}}}$	127.0–156.2
4 (P-1)	$CSiC_{ipso}$	104.6–113.3	$\mathbf{CSiC_{\mathit{ipso}}C_{\mathit{ortho}}}$	109.1–164.6

molecules are similar enough to retain the same packing structure with parallel rows of structures aligned in head-to-tail chains. Interestingly, of all these structures only compound **2** shows disorder in the six phenyl rings, possibly attributed to the larger range of bond angles and dihedral angles that the molecules can tolerate.

CONCLUSIONS

Small changes in molecular structure have the possibility of creating significant changes in molecular packing. The crystal structures of two very similar molecular gyroscopes were studied. One has a *bis*-triphenylmethyl stator (**1**) and the other has a *bis*-triphenylsilanyl analog (**2**). In addition, a structural analysis of the dimers of 3,3,3-triphenylpropyne (**3**) and triphenylsilylacetylene (**4**) was performed. The substitution of silicon for carbon increases the core molecular length by *ca.* 0.7 Å and allows for more flexibility of the bond angle and torsion angle around the sp^3 hybridized atom. Even with some relaxed geometric restrictions on the molecular angles and increased molecular length, the molecular packing of compounds **2** and **4** are very similar to those of **1** and **3**. Their packing structures retain the six-fold trityl embrace between head-to-tail parallel molecular chains. The triphenylsilyl derivatives seem to posses a slightly greater tendency for disorder, as demonstrated by the structure of **2** and the presence a large number of unique molecules in the structures of the two polymorphs of compound **4**. Solid state rotational dynamics studies of compound **2** are currently under way, preliminary results reveal that compound **2** has a significantly lower barrier for phenylene flipping than compound **1** [11].

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[10] Selected crystallographic information for compound **2**: $C_{46}H_{34}Si_2$, $MW = 642.91$, triclinic, space group P-1, $a = 8.9594(19)\,Å$, $b = 9.003(2)\,Å$, $c = 12.198(3)\,Å$, $\alpha = 99.492(4)^\circ$, $\beta = 98.721(4)^\circ$, $\gamma = 111.133(4)^\circ$, $V = 881.0(3)\,Å^3$, $Z = 1$, $\rho_{\mathrm{cald}} = 1.212\,\mathrm{Mg/m^3}$, $F(000) = 338$, $\lambda = 0.71073\,Å$, $\mu(\mathrm{Mo}\ K_\alpha) = 0.067\,\mathrm{mm^{-1}}$, $T = 100(2)$ K, crystal size $= 0.6 \times 0.3 \times 0.03\,\mathrm{mm^3}$, of the 6926 reflections collected $(2.50 \leq \theta \leq 27.08^\circ)$, 3978 [$R(int) = 0.0327$] were independent reflections; max/min residual electron density 0.529 and $-0.458\ e\,Å^{-3}$, $R1 = 0.0788$ $(I > 2\sigma(I))$ and $wR2 = 0.2227$ (all data).

[11] Karlen, S. D. & Garcia-Garibay, M. A. Unpublished data.