

**Molecular Compasses and Gyroscopes: Engineering Molecular Crystals with Fast Internal Rotation**Tinh-Alfredo V. Khuong, Gerardo Zepeda,<sup>#</sup> Rebecca Ruiz, Saeed I. Khan, and Miguel A. Garcia-Garibay\*

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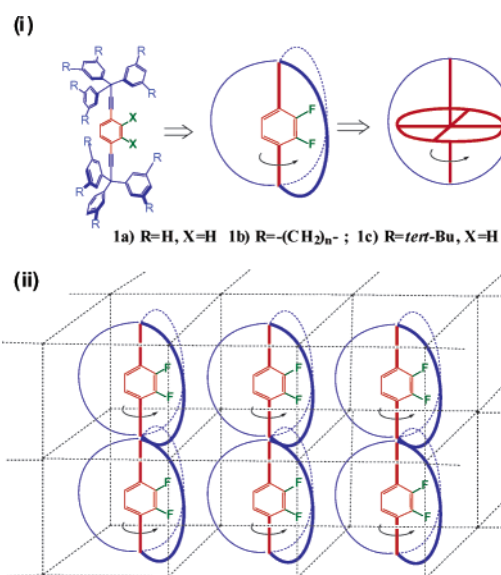
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**ABSTRACT:** Crystals of 1,4-bis[3,3,3-tri(3,4-ditertbutyl)phenylpropynyl]benzene **1c** may be viewed as a collection of molecular gyroscopes having a central *p*-diethynylphenylene as a rotary element encased by two bulky triarylmethyl groups. Single-crystal X-ray analysis, <sup>13</sup>C CPMAS NMR, and <sup>2</sup>H NMR quadrupolar-echo line-shape analysis revealed a lattice of molecules with phenylene groups experiencing rotary motion in the gigahertz regime near ambient temperature.

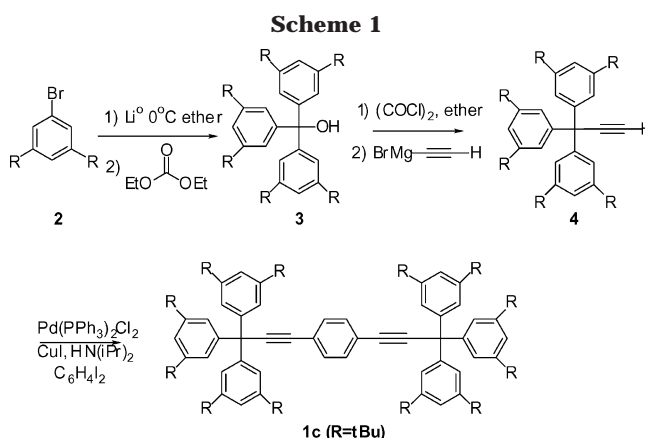
While structural aspects of crystal engineering have enjoyed a great deal of attention in recent years,<sup>1</sup> studies aimed at a better understanding and control of molecular motion in crystals have been comparatively scarce.<sup>2</sup> With that in mind, we recently suggested a promising approach based on molecules possessing rigid, encapsulating structures that support highly mobile parts, even in a close-packed environment (Figure 1).<sup>3</sup> By form and function, these molecules resemble macroscopic *compasses* and *gyroscopes*. They consist of a 1,4-diethynylphenylene (in red) linked to nonpolar triarylmethanes<sup>3</sup> or triptycenes<sup>4</sup> (in blue). Ideally, fast rotation of the phenylene group is facilitated by the nearly barrierless motion about alkyne–aryl bonds<sup>5</sup> and by the shielding provided by the triphenylmethanes (or triptycenes), which can act as an encapsulating framework.

While compounds possessing polar rotors (e.g., **1a**, X = F) are expected to have interesting dielectric properties,<sup>3</sup> the first and most basic molecular gyroscope was prepared merely to develop a convenient synthetic strategy. Surprisingly, 1,4-bis(3,3,3-triphenylpropynyl)benzene **1a** [Figure 1(i), R=X=H] was found to undergo 180° phenylene flips at an approximate rate of 6 kHz at 298 K and to have a rotational barrier of ca. 12.8 kcal/mol in solvated crystals from benzene. An identical process with a slightly higher barrier (14.6 kcal/mol) was also observed in solvent-free crystals grown from CH<sub>2</sub>Cl<sub>2</sub>. Although these appear to be the fastest flipping phenylenes recorded in a crystalline solid,<sup>6</sup> steric hindrance arises from nearest neighbors and from solvent molecules in the crystal.<sup>3</sup> To facilitate the rotation of the central phenylene, a greater degree of steric shielding is required. This may be accomplished by installing bridging chains (**1b**) or sufficiently bulky groups (**1c**). Molecular models suggest that adequate steric encapsulation may be achieved with *tert*-butyl groups at the two *meta* positions of each phenyl ring in the two trityl groups [**1c**, R = *tert*-Bu, Figure 1(i)]. In this communication, we report the synthesis, crystal structure, and solid-state dynamics of the dodecakis-*tert*-butyl compound **1c**. Remarkably, the phenylene rotor of **1c** undergoes a 2-fold flipping motion with rates in excess of 100 MHz (10<sup>8</sup> Hz) in the solid state at ambient temperature.

Compound **1c** was prepared from 3,5-di-*tert*-butylphenylbromide **2** as illustrated (Scheme 1).<sup>7</sup> Alcohol **3** was obtained in 82% yield by addition of 3,5-di-*tert*-butylphenyllithium to 0.3 equiv of diethyl carbonate. The alcohol



**Figure 1.** (i) Proposed structural analogy between compound **1** and a macroscopic gyroscope. (ii) Representation of a hypothetical crystal where individual molecules exhibit gyroscopic motion or compass-like alignment.

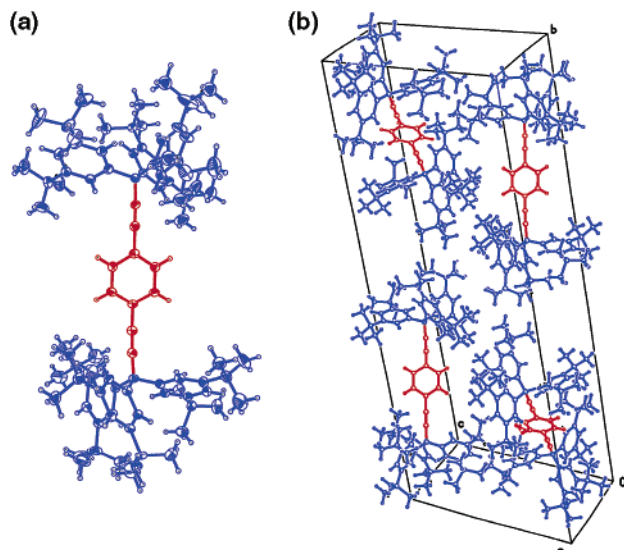


was converted to tritylacetylene **4** in 89% yield by reaction of an intermediate trityl chloride with 3 equiv of 0.5 M ethynylmagnesium bromide in THF.<sup>7,8</sup> The final coupling reaction was performed with 5% Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 10% CuI<sup>9</sup> to yield **1c** in 64% yield.

X-ray quality plates of **1c** were obtained as a CH<sub>2</sub>Cl<sub>2</sub> solvate by slow evaporation from a 10:2:1 mixture of

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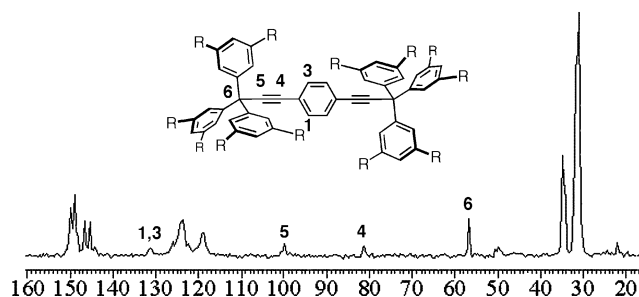
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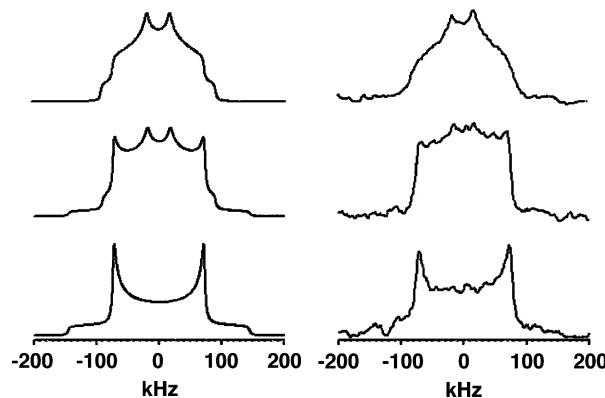
**Figure 2.** (a) ORTEP diagram of molecular gyroscope **1c** at 30% probability. (b) Unit cell illustrating the packing arrangement of **1c** with solvent molecules excluded.

pentane,  $\text{CH}_2\text{Cl}_2$ , and MeOH. Although these crystals retained their shape indefinitely, they became opaque upon standing in air for a few hours due to loss of solvent of crystallization. The structure was solved by direct methods in the monoclinic space group  $P2_1/n$  with a molecule of **1c** and two  $\text{CH}_2\text{Cl}_2$  per asymmetric unit.<sup>10</sup> The molecular structure is characterized by having the two trityl groups in propeller conformations with opposite configurations, the triple bonds nearly collinear, and the *tert*-butyl groups presenting some disorder (Figure 2a). Molecules in the crystal have their long axis close to the crystallographic *b*-direction, with a  $46.9^\circ$  angle between each other (Figure 2b). Two disordered  $\text{CH}_2\text{Cl}_2$  molecules per molecular gyroscope are omitted in Figure 2b for clarity. One acts as a space-filler between the trityl groups of adjacent molecules, and the other is located close to the central phenylene (see below). While the anisotropic thermal parameters of most *tert*-butyl groups indicate local motion or disorder, those of the central phenylene are relatively small and nearly spherical. Qualitatively, this suggests that there is little or no rotation about the 1,4-axis of the central rotor at 100 K, or that there are rapid  $180^\circ$  ring flips with a well-defined energy minimum.

Prior to studying the motion of the phenylene group in crystals of **1c** by  $^{13}\text{C}$  and  $^2\text{H}$  NMR, we set out to determine the structural integrity of the lattice as a function of temperature. Even while carefully handled, crystals of **1c** lost the solvent of crystallization when samples were ground for solid-state NMR and differential scanning calorimetry (DSC). Thermal analysis revealed a sharp melting transition at  $335^\circ\text{C}$ , indicating the crystallinity of the desolvated phase. The  $^{13}\text{C}$  NMR spectra obtained with cross-polarization and magic angle spinning (CPMAS) showed no signals corresponding to  $\text{CH}_2\text{Cl}_2$ . However, relatively sharp spectra supported the notion that the lattice had not collapsed into an amorphous solid, but that it had maintained, at least partially (see below), crystalline order (Figure 3). The first indication of fast phenylene rotation at ambient temperature was obtained with  $^{13}\text{C}$  CPMAS NMR spectra collected with a nonquaternary suppression pulse sequence.<sup>11</sup> In addition to the expected signals from the quaternary carbon atoms and rapidly rotating methyl groups, the spectrum showed a strong signal at 132 ppm, which is assigned to C1 and C3 of the rapidly rotating phenylene.



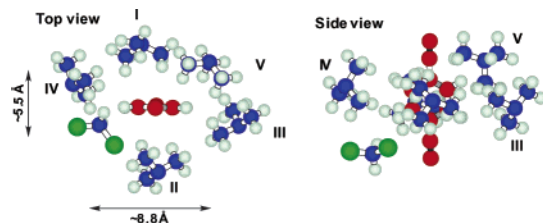
**Figure 3.**  $^{13}\text{C}$  CP-MAS NMR spectra of molecular gyroscope **1c** obtained from desolvated crystals. Dipolar dephasing experiments were used to confirm the assignment of nonprotonated and highly mobile signals, including the phenylene signal at C1, C3.



**Figure 4.** Calculated (left column) and experimental (right column) quadrupolar echo solid state  $^2\text{H}$  NMR measured at 293 (top), 213 (middle), and 193 K (bottom).

To determine the symmetry of phenylene rotation and expecting to measure its rate constant and activation energy with quadrupolar echo solid state  $^2\text{H}$  NMR, we prepared and crystallized samples of **1c** with a deuterated phenylene. The orientation-dependence of the quadrupolar coupling in  $^2\text{H}$  NMR makes it one of the most sensitive probes for dynamics in crystalline solids and rigid media.<sup>6,12</sup> While powder samples with slowly moving or rigid molecules give rise to broad symmetric spectra known as Pake patterns, molecular motion and reorientation give rise to spectral variations that depend on the dynamics and symmetry of the deuteron motion. The dynamic range covered by line shape analysis techniques varies from ca.  $10^4$  to  $10^8\text{ s}^{-1}$ , which correspond to the slow and fast exchange limit, respectively. For our studies, we take advantage of the well-characterized spectral changes occurring upon 2- and 3-fold phenylene flipping as well as free phenylene rotation about its 1,4-axis.<sup>6,13,14</sup> Spectra were obtained from 333 to 193 K at 46.07 MHz with a  $90^\circ$  pulse width of  $2.25\text{ }\mu\text{s}$ , and with echo and refocusing delays of 50 and  $40\text{ }\mu\text{s}$ , respectively. The delay between pulses was varied between 6 and 18 s, with the longest delay necessary for relaxation at the lower temperatures.

With motion restricted along the 1,4-axis, spectra should be ideally fit by simulating the symmetry of rotation and the characteristic rate of motion. For a given rate constant in the fast and intermediate exchange, readily distinguishable spectra are expected for 2-fold, 3-fold, and continuous rotation models. Spectra measured with desolvated **1c** above ca. 293 K were satisfactorily fit to rates of rotation corresponding to the fast exchange limit  $k_{\text{rot}} > 10^8\text{ s}^{-1}$  (Figure 4, top). Spectra collected at 193 K and below gave a full Pake pattern corresponding to the slow-exchange limit with  $k_{\text{rot}} < 10^3\text{ s}^{-1}$  (Figure 4, bottom). Spectra measured at intermediate temperatures (273–213 K) could



**Figure 5.** Top and side views of the local environment around the phenylene rotor (in red) of molecular gyroscope **1c** showing five *tert*-butyl groups (I–V) from adjacent molecules (in blue) and one molecule of methylene chloride (chlorine shown in green, please see text).

not be fit with a single rate constant in the intermediate exchange region ( $10^4$ – $10^6$  s $^{-1}$ ), a surprising result implying a heterogeneous sample. Although samples **1c** appeared crystalline and homogeneous, the  $^2\text{H}$  NMR results demand the coexistence of molecules in fast ( $\geq 10^8$  s $^{-1}$ ) and slow ( $\leq 10^3$  s $^{-1}$ ) exchange regimes. Although the spectrum shown in the middle part of Figure 4 could be reproduced by a simplistic model that includes 1:1 contributions of fast and slow components, fitting models involving a broad distribution of rate constants may not be discarded.<sup>6a,b</sup> Spectra corresponding to the intermediate exchange regime have significantly lower intensities, and their contribution may not be evident in the presence of the more intense kinetic components. In earlier studies of phenylene motion in polymers by Spiess et al., glassy samples of bisphenol A-polycarbonate were fit by a log-Gaussian distribution of correlation times weighed by a corresponding distribution of intensities.<sup>6</sup> Indeed, evidence that solid samples of **1c** contain amorphous and crystalline components was obtained with samples that were melted and allowed to resolidify. Spectra measured at temperatures where fast motion had been previously observed (193–333 K) corresponded now to the slow exchange regime as expected for a collapsed lattice in an amorphous sample.

While it was not possible to determine a unique activation barrier for **1c**, an approximate rate increase of at least 5 orders of magnitude at ambient temperature with **1c** as compared to the parent compound **1a** is a step in the right direction. Although the loss of  $\text{CH}_2\text{Cl}_2$  prevents us from drawing firm conclusions, we have analyzed the packing structure of **1c** (Figure 5) with the hope of gaining insight for the construction of improved “molecular gyroscopes”. The closest *intramolecular* contacts between hydrogens in a phenylene rotor and hydrogens in the *tert*-butyl groups occur at distances of 3.14, 3.25, 3.44, and 3.68 Å. All of these distances are significantly larger than twice the van der Waals radius of hydrogen (1.20 Å),<sup>15</sup> suggesting that intramolecular interactions should not hinder the rotation of the central phenylene. Remarkably, despite the large steric bulk provided by 12 *tert*-butyl groups, adjacent molecules fill in much of the space around the phenylene rotor by interdigitation. A cross section perpendicular to the phenylene 1,4-axis with the closest-neighboring groups shows a roughly elliptical cavity of ca.  $5.5 \times 8.8$  Å, which accounts for an energy minimum indicated by the 180° flipping motion (Figure 5). Free volume around the phenylene rotor is limited. Each of the four hydrogens atoms in the rotor has 4–5 hydrogens from neighboring *tert*-butyl groups less than 3.0 Å apart. There is one intermolecular H–H close contact at 2.23 Å, which is below the sum of their van der Waals radii of 2.4 Å, and one of the hydrogen atoms in the phenylene rotor is very close (2.34 Å) to a molecule of methylene chloride. Assuming that the local phenylene structure in the desolvated crystal is similar to that in Figure 5, one should not expect rapid rotation if

the structure were rigid as the central phenylene would encounter prohibitive steric contacts with *tert*-butyl groups labeled I and II. We suggest that phenylene rotation may require a periodic oscillatory motion that changes the dimensions of the ellipsoidal cavity, perhaps in concert with a lattice vibration.

In conclusion, **1c** is the first compound specifically engineered to undergo rapid rotation in a crystalline solid. Although the steric shielding provided by 12 *tert*-butyl groups on the 1,4-bis(triphenylpropynyl)benzene framework improve the 2-fold rotational motion of the phenylene group from the megahertz regime in **1a** to the gigahertz regime in **1c**, it should be possible to design crystals with better encapsulation of the rotary units and a more robust crystal lattice. Studies are in progress in our group to address these and other materials science related issues.

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**Supporting Information Available:** Synthesis, crystallization, spectral characterization data (PDF), and crystallographic information (CIF) of compound **1c** are available on the Internet free of charge at <http://pubs.acs.org>.

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