

Improved Physical Properties and Rotational Dynamics in a Molecular Gyroscope with an Asymmetric Stator Structure

Steven D. Karlen, Carlos E. Godinez, and Miguel A. Garcia-Garibay*

Department of Chemistry and Biochemistry, University of California,
Los Angeles, California 90095-1569

mgg@chem.ucla.edu

Received April 12, 2006

ABSTRACT



A molecular gyroscope consisting of a 1,4-diethynylphenylene rotator linked to trityl and triptycyl groups (3) showed significantly improved physical properties and faster rotational dynamics than analogous symmetric bis(trityl) (1) or bis(triptycyl) (2) structures. An activation energy of 7.9 kcal/mol for 3 was determined by ^2H NMR. This is ca. 4–6 kcal/mol lower than that of compound 1. The different dynamics of the three compounds can be qualitatively understood in terms of their different packing coefficients.

Recent interest in the field of artificial molecular machines has been focused on the creative design of molecular analogues to macroscopic objects. These systems have been studied in solutions,¹ on surfaces,² and in polymers.³ With the purpose of engineering molecular motions in crystals,⁴

we have recently investigated a series of compounds with structural attributes analogous to those of macroscopic gyroscopes.⁵ As illustrated in Figure 1, many of these structures consist of a *para*-diethynylphenylene acting as the rotator and axle (shown in red) and two bulky triptycyl ($\text{X} = \text{CH}$)⁶ or triarylmethyl ($\text{X} = \text{H,H,H}$)⁷ groups acting as a shielding stator (shown in blue).⁸

(1) (a) Mislow, K. *Chemtracts: Org. Chem.* **1988**, 2, 151–174. (b) Bedard, T. C.; Moore, J. *J. Am. Chem. Soc.* **1995**, 117, 10662–10671. (c) Kelly, T. R. *Acc. Chem. Res.* **2001**, 34, 514–522. (d) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines – A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003. (e) Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. *Science* **2005**, 310, 80–82. (f) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, 242, 174–179. (g) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, 34, 477–487.

(2) (a) Hernandez, R.; Tseng, H.-R.; Wong, J. W.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2004**, 126, 3370–3371. (b) Steuerman, D. W.; Tseng, H.-R.; Peters, A. J.; Flood, A. H.; Jeppesen, J. O.; Nielsen, K. A.; Stoddart, J. F.; Heath, J. R. *Angew. Chem., Int. Ed.* **2004**, 43, 6486–6491. (c) van Delden, R. A.; ter Wiel, M. K. J.; Pollard, M. M.; Vicario, J.; Koumura, N.; Feringa, B. L. *Nature* **2005**, 437, 1337–1340. (d) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, 05.

(3) (a) Marsella, M. J.; Reid, R. J.; Wang, L.-S. *Polym. Mater. Sci. Eng.* **2001**, 85, 474. (b) Hugel, T.; Holland, N. B.; Cattani, A.; Moroder, L.; Seit, M.; Gaub, H. E. *Science* **2002**, 296, 1103–1106.

(4) (a) Karlen, S. D.; Garcia-Garibay, M. A. *Amphidynamic Crystals: Structural Blueprints for Molecular Machines*. In *Molecular Machines*; Kelly, T. R., Ed.; Topics in Current Chemistry Series V. 262; Springer-Verlag: Berlin, 2005; pp 179–227. (b) Garcia-Garibay, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, 102, 10771–10776.

(5) For elegant synthetic work on molecular gyroscopes, see also: (a) Shima, T.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2004**, 43, 5537–5540.

(6) Godinez, C. E.; Zepeda, G.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, 124, 4701–4707.

(7) (a) Dominguez, Z.; Dang, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, 124, 2398–2399. (b) Dominguez, Z.; Khuong, T.-A. V.; Dang, H.; Sanrame, C. N.; Nunez, J. E.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2003**, 125, 8827–8837. (c) Dominguez, Z.; Dang, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, 124, 7719–7727.

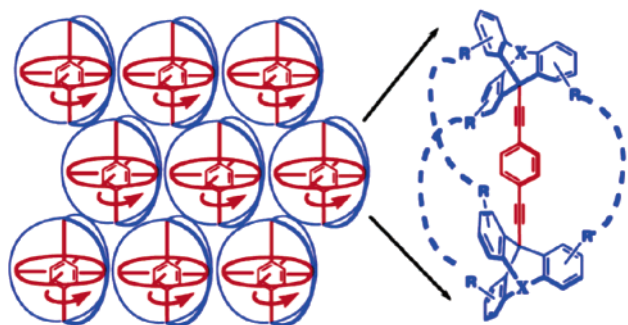
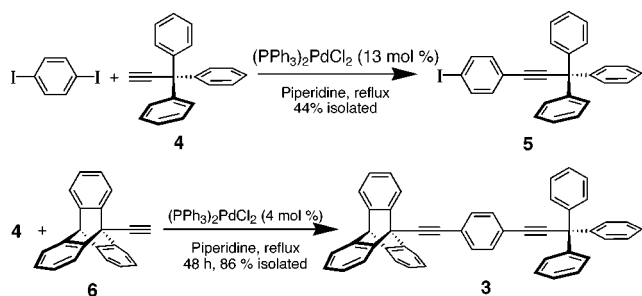


Figure 1. Molecules with structural attributes reminiscent of macroscopic gyroscopes may be constructed with trityl (X = H,H,H) and or triptycyl (X = CH) groups.

With studies centered on variations on the triptycyl or trityl groups, we have shown that changes in the structure of the stator may have a dramatic effect on the physical properties and rotary dynamics. For example, the parent bis(trityl) (**1**) and bis(triptycyl) (**2**) structures (Scheme 1) have a tendency

Scheme 1



to crystallize with solvent, and having rigid, rod-shaped structures, all molecules align in the same direction in low-symmetry crystals. However, molecular gyroscope **1** is soluble in most organic solvents and melts at 316 °C whereas compound **2** dissolves only in hot aromatic solvents (e.g., xylenes and chlorobenzene) and forms crystals that decompose without melting above 400 °C.

The crystal structures of **1** and **2** also differ by their packing coefficients, a measure of the amount of empty volume in the structure. The packing coefficient C_k is given by the volume of all the molecules in the unit cell relative to the total cell volume ($C_k = V_{\text{mol}}/V_{\text{cell}}$).^{9,10} For organic compounds, they typically vary between 0.65 and 0.80. With $C_k = 0.69$ and $C_k = 0.85$ for **1** and **2**, respectively, it is not surprising that the phenylene group of the bis(trityl) com-

pound rotates by 180° and flips at a rate of ca. 1.3 MHz at 65 °C while the phenylene group of the bis(triptycyl) analogue **2** is static.

Considering the remarkable differences in physical and dynamic properties of **1** and **2** and knowing that a hybrid structure would severely compromise the packing motif of either component, it was of interest to investigate molecular gyroscope **3** with a mixed trityl–triptycyl stator (Figure 2).

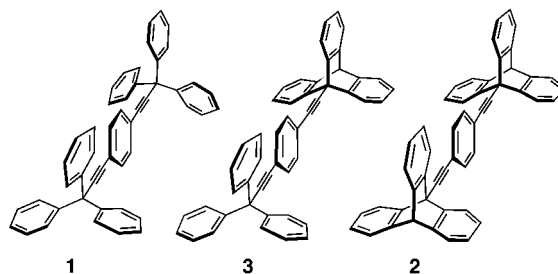


Figure 2. Molecular gyroscopes consisting of a 1,4-diethynylphenylene rotator linked to trityl and triptycyl groups (**3**), symmetric bis(trityl) (**1**), and bis(triptycyl) (**2**) stators.

We reasoned that a hybrid structure could have the desirable sturdiness of **2**, the good solubility of **1**, and the rapid dynamics potentially associated with a lower-density crystal.

The desired molecular gyroscope **3** was prepared in two steps (Scheme 1) by Pd(0)-coupling reactions among diiodobenzene, 1,1,1-triphenylpropyne **4**, and 9-triptycyl acetylene **6**. We opted for two sequential coupling steps rather than one to prevent a statistical mixture of products. To minimize the formation of **1** during the preparation of compound **5**, 2 equiv of diiodobenzene was used per equiv of **4**. As expected, the hybrid structure **3** possessed the solubility associated with **1**, being readily soluble in common organic solvents such as methylene chloride, chloroform, benzene, etc. The ¹H and ¹³C NMR spectra of **3** in solution closely resemble a combination of the spectra from the two symmetric structures, including a central phenylene characterized by an A₂B₂ ¹H spin system and four easily distinguishable alkyne carbons in the ¹³C NMR. Molecular gyroscope **3** formed crystals with a visually determined melting point of 305 °C, which is close to the melting point of the bis(trityl) analogue **1** of 316 °C.⁷ Although compound **3** has a tendency to form microcrystalline solids from several solvents, we were able to obtain X-ray quality single crystals by slow evaporation from chloroform. These crystals turned out to be a solvent clathrate (Figure 3), as it is commonly observed for the structures of both **1** and **2**.⁴ Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis of the clathrate showed the gradual loss of chloroform between 50 and 100 °C followed by melting at 305 °C. The broad range of chloroform loss, extending to temperatures well above its boiling point (61 °C), suggests that solvent molecules are held tight within the crystal lattice.

The structure of the chloroform clathrate of **3** was solved in the triclinic space group $P\bar{1}$.¹¹ The asymmetric unit

(8) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281–1376.

(9) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

(10) Molecular volumes were calculated using the group increment approach with the values reported in: Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220–5225.

includes one molecule of **3** and one molecule of chloroform. The diethynylphenylene of **3** has a relatively sharp bend (Figure 3), with an angle of 170.76° from the quaternary

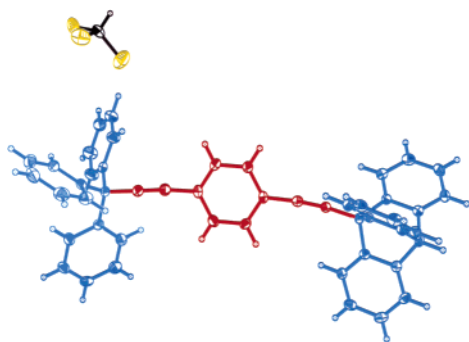


Figure 3. ORTEP diagram of molecular gyroscope **3** with thermal ellipsoids shown at 50% probability.

carbon of the trityl group to the center of the phenylene to the bridgehead carbon of the triptycene. As in the case of **1** and **2**, molecular gyroscope **3** packs in a parallel alignment, as illustrated in Figure 4. With a feature reminiscent of the packing of **2**, a face-to-face interaction between the phenylene rotator of one molecule and the benzene of a neighboring triptycene leads to a close contact (3.376 \AA) between alkyne and triptycene carbons (Figure 4, top). When viewed along the normal of the $(0,1,-1)$ plane, molecules of **3** pack with trityl and triptycene groups aligned in alternating directions (Figure 4, bottom). There are several close contacts in the structure. Among these, the chloroform hydrogen is positioned near the center of one of the benzene rings of a triptycene, with distances to four of the benzene carbons varying between 2.533 and 2.842 \AA (Figure 4, bottom).

The stability of the solvate was first evaluated under the conditions of cross polarization–magic angle spinning (CP–MAS) NMR measurements at ambient temperature. The solid-state ^{13}C CP–MAS NMR spectra agreed qualitatively well with the spectrum obtained in solution. As shown in the top of Figure 5, signals corresponding to the quaternary triptycyl carbons at 53 ppm are well resolved from the quaternary trityl carbon at ca. 56 ppm . However, chloroform and alkyne signals between 75 and 100 ppm are not consistent with a pure crystallographic phase and a unique molecule per asymmetric unit, suggesting that structural heterogeneity arises as a result of desolvation. Complete conversion of the CHCl_3 clathrate to a solvent-free form was accomplished by keeping the former at 110°C for 2 days. The ^{13}C CP–MAS NMR spectrum obtained after this

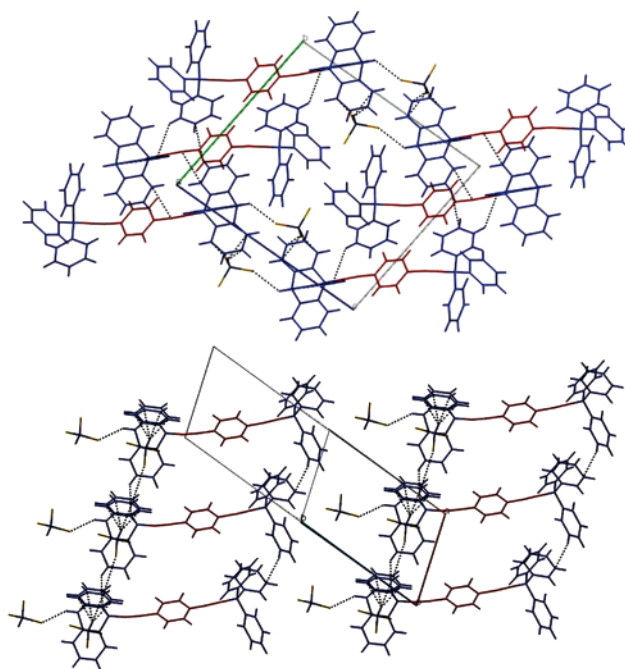


Figure 4. Molecular packing of chloroform clathrate of **3** (top) viewed normal to the $(1,0,0)$ plane and (bottom) normal to the $(0,1,-1)$ plane. Close contacts between neighboring molecules are indicated with dotted lines.

treatment revealed the loss of solvent signals at 75 ppm along with major changes in every region of the spectrum. We were able to confirm that the resulting solvent-free phase is crystalline by a sharp X-ray powder diffraction (Supporting Information).

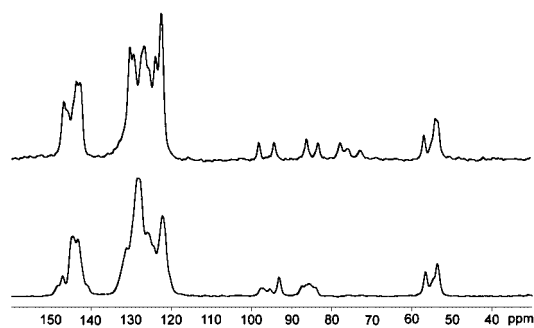


Figure 5. (Top) ^{13}C CP–MAS NMR spectrum of a freshly prepared CHCl_3 clathrate of **1**. (Bottom) Solvent-free sample of **1** after removal of CHCl_3 by heating the sample to 110°C for 2 days.

(11) Selected crystallographic information for chloroform clathrate of compound **3**: $\text{C}_{49}\text{H}_{32}\cdot\text{C}_1\text{H}_1\text{Cl}_3$, $M_w = 740.11$, triclinic, space group $P1$, $a = 8.0460(14) \text{ \AA}$, $b = 14.953(3) \text{ \AA}$, $c = 16.805(3) \text{ \AA}$, $\alpha = 80.884(8)^\circ$, $\beta = 76.657(8)^\circ$, $\gamma = 75.271(8)^\circ$, $V = 1891.8(6) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.299 \text{ Mg/m}^3$, $F(000) = 768$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo K}\alpha) = 0.067 \text{ mm}^{-1}$, $T = 120(2) \text{ K}$, crystal size $= 0.40 \times 0.15 \times 0.10 \text{ mm}^3$; of the 16 000 reflections collected ($1.42 \leq \theta \leq 28.35^\circ$), 8752 [$R_{\text{int}} = 0.0400$] were independent reflections; max/min residual electron density 0.413 and $-0.512 \text{ e \AA}^{-3}$, $R1 = 0.0556$ ($I > 2\sigma(I)$) and $wR2 = 0.1455$ (all data).

Given the relative instability of the solvent clathrate and the impossibility of reliably measuring its NMR spectrum as a function of variable temperature, we decided to analyze the solid-state rotational dynamics of **3** in a desolvated sample. As in previous studies, measurements were carried out by quadrupolar echo ^2H NMR, one of the most sensitive

probes for dynamics in crystalline solids and rigid media.¹² In brief, the ^2H NMR method relies on the orientation dependence of the quadrupolar coupling and its modulation by molecular motions. Although powder samples with slowly moving or rigid molecules give rise to broad symmetric spectra known as a Pake pattern, molecular motion and reorientation give rise to spectral variations that depend on the rate and type of the deuteron motion. The dynamic range covered by line shape analysis techniques varies from ca. 10^4 to 10^8 s^{-1} , which correspond to the slow and fast exchange limits of the method, respectively. For our studies, we take advantage of the well-characterized spectral changes occurring upon rotation of phenylene groups about their 1,4-axis, typically by 180° angular displacement, which are commonly referred to as phenylene flips.^{13,14}

An isotopically labeled sample of **3**- d_4 for dynamic NMR was prepared as shown in Scheme 1 using 1,4-dibromobenzene- d_4 . The spectra were acquired with a quadrupole echo pulse sequence¹⁵ with a 90° pulse of $2.25\text{ }\mu\text{s}$, with echo and refocusing delays of 50 and $40\text{ }\mu\text{s}$, respectively. The delay between pulses was 30 s. Exchange rates were determined by visually matching the experimental data to spectra simulated using the program reported by Nishikiori et al.¹⁴ The simulated spectra were obtained using a quadrupolar coupling constant (QCC) measured from spectra acquired in the slow exchange regime and a model that considers site exchange of the ^2H nuclei by 180° rotations. The only adjustable parameter used in the simulation was the site-exchange rate k_{rot} , which was varied from 10^4 to 10^8 Hz .

The experimental and simulated spectra for the solvent-free sample are shown in Figure 6 for data recorded between 300 and 448 K. The best visual agreement was obtained using rates of rotation between 0.5×10^6 and $50 \times 10^6\text{ s}^{-1}$. Arrhenius analysis of the data gave a barrier for phenylene flipping of $7.9 \pm 1.6\text{ kcal/mol}$ and a preexponential factor of $2.75 \times 10^{11}\text{ Hz}$.¹⁶ The relatively linear plot suggests that the solvent-free structure is a single phase and not a mixture of polymorphs. Notably, the barrier in **3** is 6 kcal/mol lower than that previously measured by the same method for solvent-free samples of **1** within a similar temperature range.⁷ The lower barrier results in faster rotation rates, which are desirable to control the orientation of dipolar analogues with external electric and magnetic fields.

(12) Hoatson, G. L.; Vold, R. L. *NMR Basic Princ. Prog.* **1994**, 32, 1–67.

(13) (a) Cholli, A. L.; Dumais, J. J.; Engel, A. K.; Jelinski, L. W. *Macromolecules* **1984**, 17, 2399–2404. (b) Rice, D. M.; Wittebort, R. J.; Griffin, R. G.; Meirovich, E.; Stimson, E. R.; Meinwald, Y. C.; Freed, J. H.; Scheraga, H. A. *J. Am. Chem. Soc.* **1981**, 103, 7707–7710. (c) Rice, D. M.; Meinwald, Y. C.; Scheraga, H. A.; Griffin, R. G. *J. Am. Chem. Soc.* **1987**, 109, 1636–1640. (d) Rice, D. M.; Blume, A.; Herzfeld, J.; Wittebort, R. J.; Huang, T. H.; DasGupta, S. K.; Griffin, R. G. *Biomol. Stereodyn. Proc. Symp.* **1981**, 2, 255–270.

(14) Nishikiori, S.; Soma, T.; Iwamoto, T. *J. Inclusion Phenom.* **1997**, 27, 233–243.

(15) The ^2H NMR spectra were acquired on a Bruker Avance spectrometer at a frequency of 46.073 MHz with a single channel solenoid probe containing a 5 mm insert. Measurements were made from 300 to 448 K with the temperature calibrated using a ^{195}Pb shift standard.

(16) The uncertainty in the barrier was estimated from simulations with the highest and lowest exchange rates that reasonably matched the experimental spectra at each temperature value.

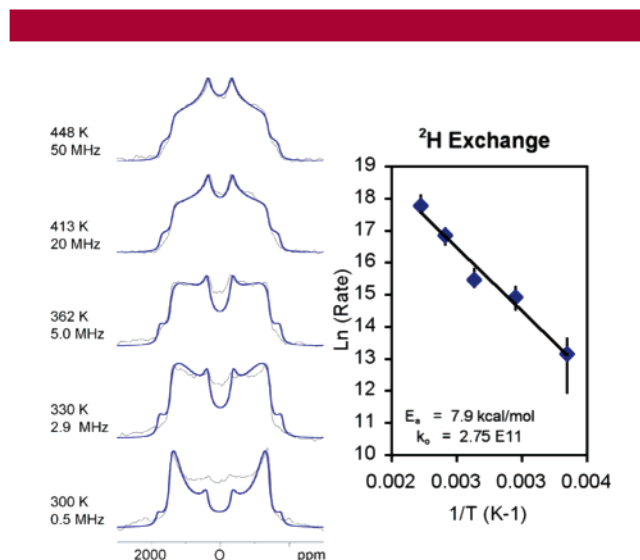


Figure 6. (Left) Experimental (thin line) and simulated (thick line) wide-line ^2H NMR spectrum of **1** in a solvent-free structure. (Right) Arrhenius plot of the exchange data.

Although we do not know the structure of solvent-free **3**, we note that this interesting result is consistent with the smaller packing coefficient for the solvated crystals of hybrid structure **3** (0.69) as compared to those of the trityl compound **1** (0.74) and the static triptycyl compound **2** (0.85). Interestingly, although an attempt to measure the ^2H NMR of the solvate gave a heterogeneous spectrum with two or more crystalline components, we made a qualitative observation that the rates of phenylene motion in the solvate are slower than those of the solvent-free structure, suggesting that desolvation occurs without collapse of the lattice (Supporting Information).

In conclusion, molecular gyroscope **3** with an asymmetric triptycyl–trityl stator structure retains the relatively high melting point of the two symmetric structures, **1** or **2**, but it displays largely improved solubility and dynamic properties. The packing structure of the CHCl_3 clathrate retains the parallel alignment observed in both **1** and **2**, with phenylene–tritycene intermolecular contacts similar to those present in **2**. We believe that compound **3** represents an interesting lead that highlights the potential properties of solid-state molecular gyroscopes with asymmetric structures.

Acknowledgment. This work was supported by the National Science Foundation through grants DMR0307028 and DGE–0114443 (NSF IGERT: Materials Creation Training Program (MCTP)).

Supporting Information Available: Synthesis and characterization of compounds **3** and **5**, TGA traces, ^2H NMR of partially desolvated samples, and crystallographic information (CIF) for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL060894D