Effects of Rotational Symmetry Order on the Solid State Dynamics of Phenylene and Diamantane Rotators

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The potential of controlling rotary dynamics at the molecular level has been recognized by several authors.[1,2] In that context, we have been interested in structures that emulate macroscopic gyroscopes while in the rigid environment of their crystalline solids.[3,4] Up to now, these have been constructed with phenylene rotators linked by dialkynyl axles to bulky triarylmethanes (trityls) or triptycenes.[4] Using solid state ^{2}H NMR, we have shown that the rotary dynamics depend primarily on steric shielding. While structures with simple triptycyls are static, molecular gyroscopes with trityl groups display 180° rotation[5] with rates of ca. 500 Hz at 300 K, and compounds with *tert*-butyl-substituted trityl frames reach rates that are >100 MHz at the same temperature[6] (Figure 1).

Though readily accessible, phenylenes have some limitations as rotary units. As the shapes of rotators tend to be well-matched by their environment, flattened phenylenes tend to have relatively high-energy barriers with rotational potentials characterized by two energy minima connected by angular displacements of 180. In contrast, more cylindrical groups with higher rotational symmetry order (Cn, $n > 2$) will have energy profiles with n minima, lower barriers, 360°/n angular displacements, and n states that may be potentially addressed with external stimuli if a permanent dipole is introduced in the structure. On our way to construct molecular gyroscopes with these characteristics, samples of 4,9-bis(4-iodophenyl)diamantane **3** became available from another study. Appreciating that diphenyldiamantane would be an ideal test system, we set out to prepare compound **6** to determine the solid state dynamics of the two groups.

Illustrated in Scheme 1, a remarkably efficient and selective phenylation of diamantane **1** was accomplished in the presence of a sludge catalyst consisting of HBr-*t*BuBr. 2,8-Diphenyldiamantane **2**, obtained as a white crystalline solid, was treated with CF₃COOI in CHCl₃ to yield the bis(*p*-iodophenyl) derivative **3** in 78% yield (mp = 344 °C). In the last step, compound **6** (mp = 334 °C) was obtained in 40% isolated yield after a Pd(0)-catalyzed coupling reaction of diiodide **3** with the previously reported trityl acetylene **5**.[3]

Thin crystals of **6** with a strong tendency for twinning were obtained from C₂H₄Cl₂–MeCN. The structure was solved in the P_{bcn} space group with half a molecule per asymmetric unit due to coincident molecular and crystallographic inversion centers (Figure 2). The packing of **6** is characterized by trityl–trityl interactions in the form of 4-fold phenyl embraces[7] leaving the phenylene–diamantane rotators arranged in layers.

To probe the rotary dynamics of phenylene and diamantane groups, we decided to explore the use of variable temperature ^{13}C CPMAS NMR coalescence and ^{1}H spin–lattice (T_1) relaxation, respectively. The dynamic range of the coalescence method varies from ca. 10²–10³ s⁻¹, and that of T_1 probes dynamic processes
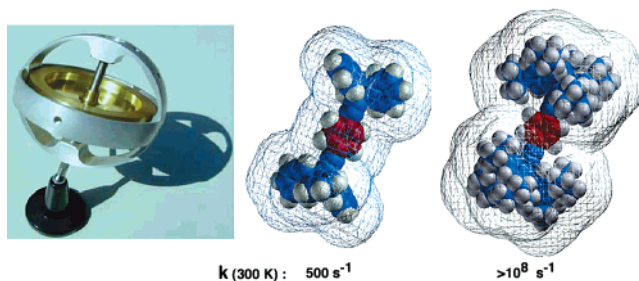
Figure 1. (Left) Macroscopic gyroscopes contain a freely rotating group inside a rigid frame. (Center and Right) Molecular gyroscopes possess a rotary group (red) and bulky shielding groups (blue) that protect the rotator. Exchange rates at 300 K are illustrated at the bottom.
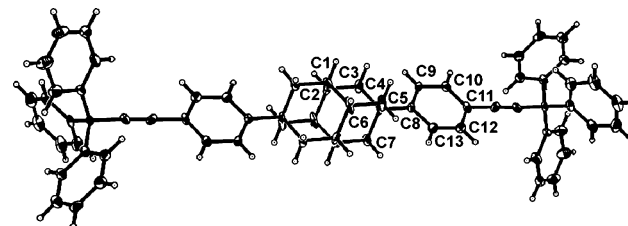
Figure 2. Ortep drawing of **6**. Only half a molecule (numbered atoms) is needed to describe the contents of the unit cell.

Scheme 1
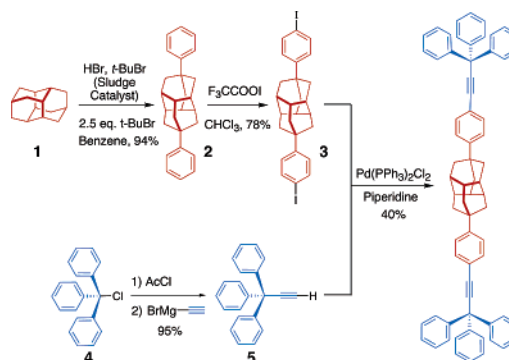


near the spectrometer frequency (300 MHz in our case). The dissimilar dynamics of the two rotators were first observed by comparison of a normal ^{13}C CPMAS spectrum and one acquired with dipolar dephasing at 25 °C (Figure 3). While nearly complete removal of the Ar–H signals by 130 ppm in the bottom spectrum is expected for static or slow moving phenyl and phenylene groups, the strong diamantane signals at 35–45 ppm (Diad-H) are indicative of fast rotation within the time scale of dipolar dephasing (ca. 50 µs).[8]

A strong overlap of trityl and phenylene signals makes it impossible to carry out a coalescence analysis. However, by using a sample of **6**-d_{30} with perdeuterated trityl groups and a short [1]H→[13]C contact time,[9] we were able to "isolate" the signals of the
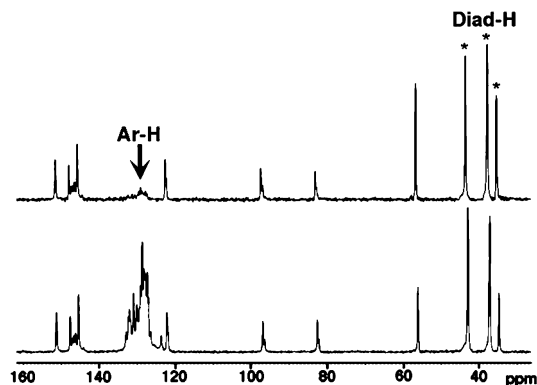
Figure 3. Normal ^{13}C CPMAS spectrum of **6** with a contact time of 10 ms (bottom), and with a 50 μs dipolar dephasing delay (top).
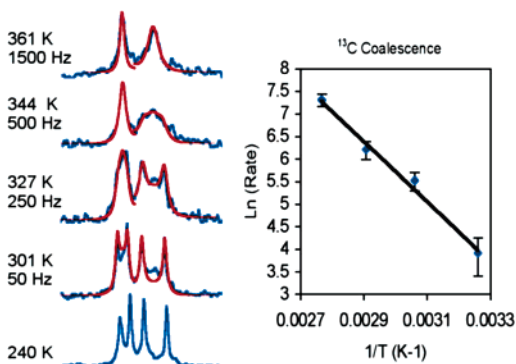
Figure 4. (Left) Experimental (blue) and simulated (red) phenylene signals showing the temperature and assumed site-exchange rates. (Right) Arrhenius plot of the coalescence data.

phenylene carbons (Figure 4). Spectral changes characteristic of coalescence processes were observed between 240 and 361 K (Figure 4). The experimental spectra were simulated with a model that exchanges the two carbon signals at 123.78 and 128.21 ppm, and at 130.85 and 132.88 ppm, with rates that vary from ca. 50−1500 Hz. An activation energy of 13.7 ± 1.1 kcal/mol and a pre-exponential factor of $(5.1 ± 4.5) \times 10^{11}$ s^{-1} were determined by Arrhenius analysis.

To determine the rotation rates and activation parameters for the diamantane rotator, we carried out ^{1}H spin−lattice relaxation measurements (T_1) by the inversion recovery method using ^{13}C CPMAS detection. It is well-known that spin−lattice relaxation in solids can be dominated by the modulation of dipolar interactions caused by reorientation of CH$_3$, NH$_3$, and other groups.[10] If a given dynamic process with a characteristic correlation time τ_c is responsible for T_1 relaxation, one can determine its activation parameters (eq 1) by fitting the measured T_1 as a function of temperature to the Kubo−Tomita relationship (eq 2), where C is a constant that depends on the number of H atoms, and ω is the spectrometer frequency.[10,11]

$$t_c = t_o \exp (E_a/kT) \qquad (1)$$

$$T_1^{-1} = C \left[\tau_c \left(1 + \omega^2 \tau_c^2 \right)^{-1} + 4 \tau_c \left(1 + 4 \omega^2 \tau_c^2 \right)^{-1} \right] \quad (2)$$

The results of inversion recovery measurements between 233 and 410 K showed that all the signals relax with a single exponential T_1 value. Variations in T_1 as a function of temperature followed the expected dependence, with the fastest relaxation (shortest T_1) at 373 K (Figure 5). An excellent fit of the experimental data revealed an activation energy E_a = 4.1 kcal/mol and a pre-
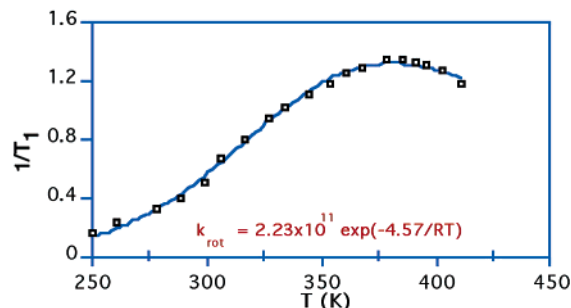
Figure 5. Experimental results (squares) and curve Kubo−Tomita fit (line) of the ^{1}H spin−lattice relaxation values from compound **6** at 300 MHz.

exponential factor $t_o = 2.2 \times 10^{11}$ s^{-1}. Notably, an AM1 calculation of the gas phase barrier with a reference frame that considers the flanking phenylenes static gave a value of 3.2 kcal/mol. Given that the barrier for rotation of the diphenylene−diamantane along the dialkyne axis should be negligible,[3,4,12] an experimental value of 4.1 kcal/mol suggests that solid state hindrance adds ~1 kcal/mol to the gas phase diamantane barrier. These observations support the notion that the more cylindrical high order rotators should have much faster rates in solids. Despite their proximity and sharing a close environment, the diamantane group rotates ca. 20 000 times faster than the phenylenes at 300 K!

Supporting Information Available: Synthesis and characterization of **1−3** and **6**, representative T_1 measurements, plot of AM1 calculations, and packing diagram (pdf). Crystallographic information of **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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