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Molecular “Compasses” and “Gyroscopes”. I. Expedient Synthesis and Solid State Dynamics of an Open Rotor with a Bis(triarylmethyl) Frame

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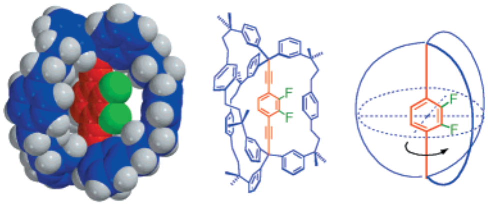
Recently, there has been a great deal of interest in the design of electrooptic materials.[1] We describe here our initial efforts toward the realization of a novel concept based on dipolar units expected to reorient under the influence of electric, magnetic, and optical stimuli. In analogy with macroscopic objects, and to suggest some of their properties and functions, we refer to these structures as *molecular compasses and gyroscopes*. The essential elements of the desired structures are illustrated with the triply bridged 1,4-bis[3,3,3-triarylpropynyl]-2,3-difluorobenzene shown in Scheme 1. The similarity between the proposed molecular structure and a gyroscope is exposed by the transformations suggested in the scheme. The analogy with a compass arises when electric or magnetic fields are considered.

The desired structures must permit the reorientation of the polar 1,4-phenylene rotor (in green and red), while maintaining the triarylmethyl (trityl) framework static in the crystal lattice (shown in blue). We expect that rotation of the phenylene group will be facilitated by the cylindrical symmetry of the alkyne units[2,3] while the trityl framework will shield the dipole from intermolecular contacts.

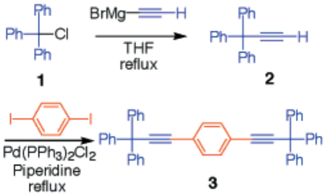
To produce the desired compounds, one needs an expedient synthesis of the 1,4-bis(triarylpropynyl)benzene framework and suitable strategies for the installation of the closing bridges. In this communication, we report a simple two-step procedure that will help solve the first synthetic problem: the parent 1,4-bis(3,3,3-triphenylpropynyl)benzene (**3**) was prepared from a readily available triphenylmethyl chloride (**1**) and 1,4-diiodobenzene (Scheme 2). Although compound **3** has an open topology, X-ray analysis revealed that it cocrystallizes with benzene in a relatively open lattice.[4] Based on variable temperature ^{13}C CPMAS NMR experiments, we were able to show that the phenylene group rotates at room temperature about the 1,4-axis in the millisecond time scale. The thermal stability of the benzene solvate was assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the rates of phenylene rotation in the desolvated crystal were determined between 297 and 385 K by ^{2}H NMR static line-shape analysis.

To prepare the open rotor **3** we first reacted trityl chloride **1** with 3 equiv of 0.5 M ethynylmagnesium bromide in refluxing THF to obtain 3,3,3-triphenylpropyne (**2**) in 80% isolated yields.[5] The desired 1,4-bis(3,3,3-triphenylpropynyl)benzene (**3**) was obtained pure in 15% isolated yield by a coupling reaction between alkyne **2** and 0.40 equiv of 1,4-diiodobenzene in the presence of 5 mol % $Pd(PPh_3)_2Cl_2$ in refluxing piperidine.[6] X-ray quality crystals were grown by slowly cooling a hot saturated benzene solution.

Scheme 1



Scheme 2



The crystal structure of rotor **3**[7] was solved in the triclinic space group $P\bar{1}$ revealing the formation of clathrate with a $\mathbf{3}:C_6H_6 = 1:2$ stoichiometry. Due to the coincidence of crystallographic and molecular inversion centers, the coordinates of one benzene and half a molecule of **3** describe the entire structure (Figure 1). The packing arrangement can be described in terms of supramolecular cages formed by four adjacent rotors (Figure 2, in blue and red) with two benzene molecules trapped inside (shown in purple). Adjacent cages interconnect to form infinite channels along the *a*- and *b*-axes. Benzene dimers experience $\pi-\pi$ stacking interactions with parallel aromatic planes at a distance of 3.52 Å and center-to-center distances of 4.88 Å. The clathrate architecture is supported by aromatic face-to-edge contacts between adjacent trityl groups, with additional interactions involving benzene molecules and phenylene groups.

In order to explore the solid state dynamics of **3** by variable-temperature ^{13}C CPMAS NMR[8,9] we had to assign all of its aromatic resonances. Since intensity losses in the CPMAS experiment occur when there are no close hydrogens for magnetization transfer,[8] assignments were made with the help of isotopic substitution (Figure 3). A sharp signal at 128 ppm (shown in purple) was assigned to the six nonequivalent carbon atoms in the benzene guest when the signal diminished in crystals grown from C_6D_6 (middle spectrum). Signals corresponding to the 1,4-phenylene (shown in red) were also confirmed by a decrease in intensity for the *ipso*- (C2, δ 122 ppm) and *ortho*-carbons (C1 and C3 δ 131 ppm) of the phenylene-d_4 (bottom spectrum). A relatively small decrease in this case was related to the efficient *intermolecular* cross-polarization contributions from the benzene guest.[10] The remaining aromatic signals, labelled in blue, were assigned to the aromatic carbons in the trityl groups. The *ipso*-carbons C7, C13, and C19 are resolved between 142 and 147 ppm and all other trityl signals are centered at 128 ppm.

The fast rotation of the 1,4-phenylene fragment at 298 K could be confirmed by low-temperature measurements, as illustrated by the splitting of the broad *ortho*-signal at δ 131 into two singlets at 131.6 and 130.8 ppm in Figure 4. With a splitting of 60 Hz between C1 and C3, and a coalescence temperature of ca. 255 K, a time

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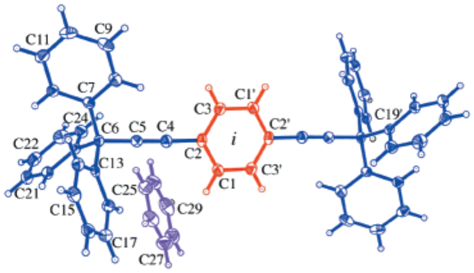

Figure 1. Ortep diagram of open rotor **3** shown with 50% probability. Colors are consistent with the packing diagram in Figure 2 and match the NMR assignment in Figure 3.

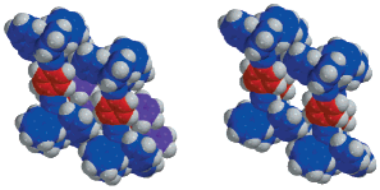

Figure 2. Left: Cluster of molecules showing rotor **3** in blue and red and benzene molecules in purple. Right: View of the same cluster with benzene molecules removed.

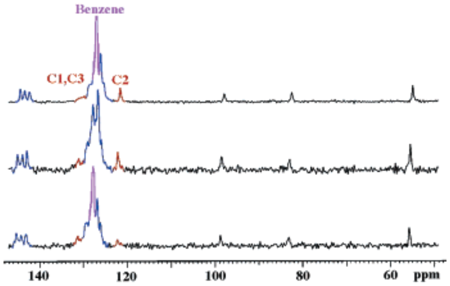

Figure 3. ^{13}C CPMAS NMR spectra of (top) rotor **3** crystallized fom C_6H_6, (middle) rotor **3** crystallized from C_6D_6, and (bottom) deuterium-labeled rotor **3**-*d*$_4$ crystallized from C_6H_6.

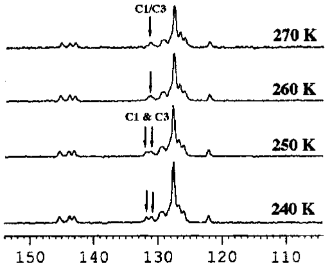

Figure 4. Variable-temperature ^{13}C CPMAS NMR with rotor **3**.

constant for rotation of 7.7 ms and an approximate barrier of 12.8 kcal/mol were calculated.

Phenylene rotation was also analyzed by quadrupolar echo ^{2}H NMR by using a model that involves 180° flips about the 1,4-axis.[11,12] Measurements with the benzene clathrate below 295 K fell within the slow exchange regime, given by an upper limit of $k_{\mathrm{rot}} < 10^4$ s^{-1}. Measurements at higher temperatures were complicated by the loss of benzene.[13] However, line-shape analysis of spectra measured with desolvated samples between 297 K and 385 K confirmed a two-fold flipping motion with rotation rates ranging between ca. 1.5×10^4 and 3.8×10^6 s^{-1} (Figure 5). The activation energy barrier for phenylene rotation calculated from this data is ca. 14.6 kcal/mol ($r^2 = 0.96$). This is about 2 kcal/mol higher than the barrier estimated in the benzene clathrate, suggesting only minor collapse of the initially porous lattice.

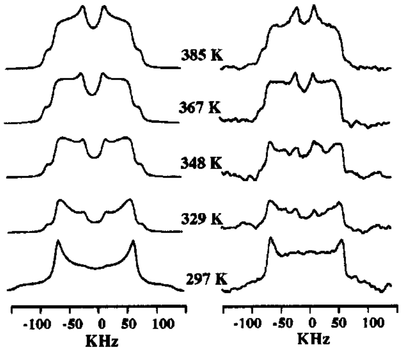

Figure 5. Experimental (right) and simulated (left) solid state ^{2}H NMR of desolvated samples of **3**-*d*$_4$. The rotation rate constants used for fitting, from bottom to top are ($\times 10^6$ s^{-1}): 0.015, 0.4, 1.3, 2.2, and 3.8.

In conclusion, we have shown that molecular frames based on alkyne linkages and trityl groups can facilitate rapid rotation of phenylene groups along their 1,4-axis. Molecular dynamics and dielectric measurements with samples prepared with polar phenylenes in molecular compasses and gyroscopes will be reported soon.

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Supporting Information Available: Stereoscopic views and X-ray data tables for rotor **3**, DSC, and TGA traces (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) For a review on related clathrate-forming structures see: McNicol, D. D.; Toda, F.; Bishop, R. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 6.

(5) Masson, J.-C.; Quan, M. L.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, *3*, 1085−1088. Yields reported by these authors were much lower.

(6) This two-step sequence works well with several trityl chlorides and aromatic halides. Several examples with full experimental details will be described in the full paper.

(7) Compound **3**: $C_{48}H_{34}{\cdot}2C_6H_6$, MW = 766.97, triclinic, space group $P\bar{1}$, a = 8.5157(19) Å, b = 9.547(2) Å, c = 14.467(3) Å, α = 77.315(4)°, β = 76.469(4)°, γ = 72.970(4)°, V = 1078.8(4) Å^3, Z = 1, ρ_{cald} = 1.181 Mg/m^3, $F(000)$ = 406, λ = 0.71073 Å, μ(Mo Kα) = 0.067 mm^{-1}, T = 100(2) K, crystal size = $0.2 \times 0.2 \times 0.1$ mm^3, of the 6884 reflections collected ($1.47 \le \theta \le 28.25°$), 4725 [$R$(int) = 0.0197] were independent reflections; max/min residual electron density 0.192 and −0.176 e Å^{-3}, $R1$ = 0.0409 ($I > 2\sigma(I)$) and $wR2$ = 0.0885 (all data).

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(12) Spectra were obtained at 46.07 MHz with a 20 μs 90° pulse, echo delays of 30 and 20 μs, and 60 s between scans. Spectra were fit assuming QCC = 180 kHz and η = 0 with the program Turbopowder (Wittebort, O.; Olejniczak, T. T.; Griffin, R. G. *J. Chem. Phys.* **1987**, *86*, 5411−5420).

(13) Desolvation occurs as a first-order phase transition at 100 °C and is closely followed by in situ recrystallization. Melting of the desolvated phase occurs at 315 °C and thermal decomposition above 400 °C.

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