Highlighting gyroscopic motion in crystals in ^{13}C CPMAS spectra by specific isotopic substitution and restricted cross polarization

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Received (in Columbia, MO, USA) 26th June 2004, Accepted 21st September 2004
First published as an Advance Article on the web 24th November 2004
DOI: 10.1039/b409744k

The temperature-dependent exchange rate and signal coalescence in the ^{13}C CPMAS NMR spectrum of a crystalline molecular gyroscope are exposed by specifically deuterating the overlapping static carbons.

Recent efforts from our group have been directed to the design, synthesis and dynamic characterization of organic structures that display internal rotary motion while in the solid state.[1,2] Some of the desired structures emulate the functions of macroscopic compasses and gyroscopes. Illustrated in Fig. 1 with 1,4-bis(3,3,3-triphenylpropynyl)benzene (**1**), they consist of a rotary group, such as a *p*-phenylene (shown in red), linked to a shielding triarylmethyl frame by a barrierless dialkyne axle (shown in blue).[1] One of the most general methods to analyze the gyroscopic motion of any central rotor in derivatives of **1** could be based on the use of coalescence analysis by variable temperature ^{13}C CPMAS NMR.[3] The coalescence method takes advantage of the crystallographic and magnetic non-equivalence of sites related by rotation about the dialkyne axis, and requires the exchanging signals to be spectrally resolved.[4] Ideally, the rates of motion are varied as a function of temperature and changes in lineshape are analyzed in terms of exchange rates.

Given that structures analogous to **1** crystallize with low molecular symmetries (either C_1 or C_i) with no less than four and as many as seven non-equivalent aromatic groups, the resolution of the carbons assigned to the phenylene rotor is difficult.[5] In order to highlight the dynamics of the rotor one may take advantage of specific deuteration to "remove" all the interfering signals from the triphenylmethyl frame.

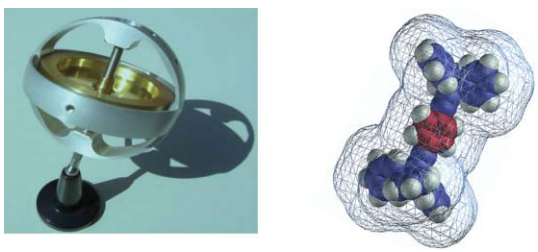

Fig. 1 (Left) A gyroscope is a device consisting of a spinning mass, or *rotor* (gold), with a spinning axis positioned through the center of the mass, and mounted within a rigid frame (silver). (Right) Analogous to the macroscopic object, molecular gyroscope **1** contains a phenylene rotor (red) with an alkyne axle and shielding groups that encapsulate it (blue).

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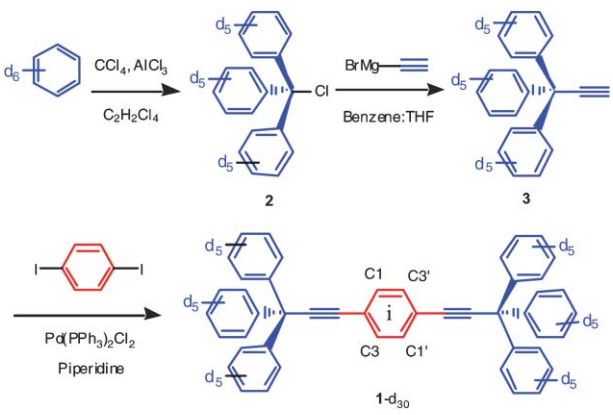
In order to implement this strategy, we developed a very simple labelling procedure and we tested the concept with relatively well-characterized crystals of compound **1**.

The synthesis of 1,4-bis(3,3,3-tri-d_5-phenylpropynyl)benzene (**1**-d_{30}) was accomplished in three steps from NMR grade d_6-benzene as indicated in Scheme 1. A simple Friedel–Crafts reaction with CCl_4 and $AlCl_3$ gave chloro-tris(d_5-phenyl)methane **2** in 76% yield.[6] The trityl chloride **2** was treated with ethynylmagnesium bromide to give 3,3,3-d_{15}-triphenylpropyne **3** in 95% yield. Finally, a double coupling with 1,4-diiodobenzene using 10% $Pd(PPh_3)_2Cl_2$ in piperidine converted alkyne **3** to **1**-d_{30} in 30% isolated yield.†

The spectroscopic and physical properties of **1**-d_{30} were consistent with those of unlabeled **1**.[1] Crystallizations occur in centrosymmetric structures (C_i) both in solvent-free crystals and in a benzene clathrate, from CH_2Cl_2 and C_6H_6, respectively. We had previously shown that the ^{13}C CPMAS NMR signals of the phenylene carbons C1 and C3 in the benzene clathrate of **1** at 131.6 and 130.8 ppm were amenable to coalescence analysis. A rate of exchange of 130 s^{-1} and a barrier of rotation of 12.8 kcal mol^{-1} were estimated at the coalescence temperature of 255 K. In contrast, measurements carried out with solvent-free crystals showed severe overlap between the carbons of the phenylene rotor and those of the triphenylmethyl groups, rendering coalescence analysis impossible.

With samples of **1**-d_{30} now available, we set out to determine its dynamics. The ^{13}C CPMAS NMR spectrum of crystals grown from CH_2Cl_2 with a contact time of 8 ms at 214 K is shown in Fig. 2 (top). The spectrum of **1**-d_{30} was analogous to that previously measured for the natural abundance samples. Signals



Scheme 1

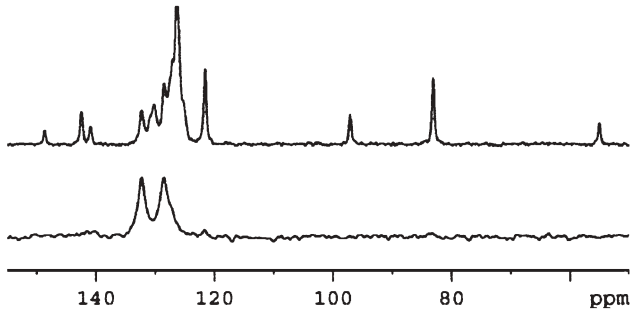


Fig. 2 ^{13}C CPMAS NMR spectrum of **1**-d_{30} with a contact time of 8 ms (top) and 50 μs (bottom). The longer contact times allow for transfer of polarization to all carbon atoms in the structure. Very short contact times only allow for polarization to the phenylene carbons, which are directly bound to the only ^{1}H in the structure.

corresponding to the saturated trityl carbons occur at 55.0 ppm and the alkyne signals at 83.7 and 97.1 ppm. The ipso-carbons from the three non-equivalent phenyl groups of the trityl frame resonate at 140.9, 142.5 and 148.6 ppm. Phenylene and protonated trityl signals overlap between 121.6 and 132.3 ppm.

It should be noted that signal intensities in the CPMAS experiment depend on the extent of ^{1}H–^{13}C cross polarization, which in the case of **1**-d_{30} originates exclusively from the ^{1}H in the central phenylene rotor. Since the strength of cross polarization depends on the distance-dependent ^{1}H–^{13}C dipole–dipole interaction,[7] signal intensities from carbons that are closer to the phenylene ^{1}H are more intense. The two alkyne signals illustrate this clearly as the carbon attached to the central ring at 83.1 ppm is twice as intense as that of the alkyne carbon at 97.1 ppm, which is one bond length further away.

When the same sample was analyzed with a contact time of 50 μs, only the signals corresponding to C1 and C3 were detected at 128.5 and 132.3 ppm (Fig. 2 bottom). Having successfully removed all the signals of the aromatic trityl group by specific deuteration, we were able to record changes in lineshape as a function of temperature (Fig. 3) between 214 and 308 K. Lineshape analysis of the isolated signals at eight temperatures was carried with the program g-NMR assuming exchange rates

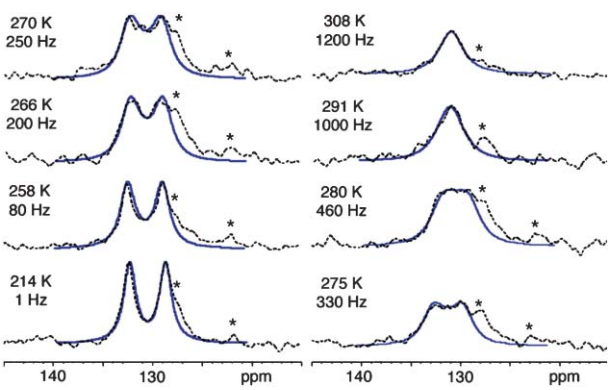


Fig. 3 Variable temperature ^{13}C CPMAS NMR of **1**-d_{30} with a contact time of 50 μs (black), simulations from g-NMR in blue. The stars indicate residual signals from the non-protonated phenylene carbon and one of the trityl signals.

between 1 and 1200 Hz.[8] Small deviations in the simulated spectra arise from contributions due to residual signals of the non-protonated phenylene carbon at 121.6 ppm and one of the trityl carbons at 126.3 ppm. These are both labelled with an asterisk in Fig. 3.

With the rate of exchange derived from the simulation and temperature data we produced an Arrhenius plot to calculate an activation barrier of 11.3 kcal mol^{-1} and a pre-exponential factor of 2.9 × 10^{11} s^{-1}. This barrier is 1.5 kcal mol^{-1} lower than that previously determined for the benzene clathrate (12.8 kcal mol^{-1}) and 3.3 kcal mol^{-1} lower than that determined for the same crystal form (E_a = 14.6 kcal mol^{-1}) using quadrupolar echo ^{2}H NMR between 300 and 480 K.[1] The differences in activation energies for the same sample with two different methods may result from the use of different temperatures, different isotopologues (**1**-d_4 *vs.* **1**-d_{30}), or the accumulated experimental errors of the two techniques. While different barriers at different temperatures would be indicative of a phase transition, an explanation based on different isotopes would reflect a well-documented steric effect arising from the different vibrational amplitudes and effective sizes of the C–^{1}H and C–^{2}H bonds.[9] While we estimate the error from the data shown in Fig. 3 to be ±1 kcal mol^{-1}, analysis of the ^{2}H NMR data published previously suggests a much larger error of ±2.5 kcal mol^{-1}. Clearly, more precise values from ^{2}H NMR experiments will be required to verify the magnitude of the suggested barrier difference.

In conclusion, a simple method was developed to prepare molecular gyroscopes with hydrogenated rotors and per-deuterated triphenylmethyl frames. Using **1**-d_{30} as a test and controlling the extent of cross polarization in the CPMAS experiment, we were able to uncover the ^{13}C signals involved in chemical exchange, revealing a coalescence process that was not detectable using samples with natural isotopic abundance.‡

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Notes and references

† Selected spectroscopic data for **1**-d_{30}, ^{1}H NMR (300 MHz): δ = 7.42 ppm (s), ^{13}C NMR (75 MHz) same as **1** except that carbon signals at δ = 128.69, 127.51, and 127.4 ppm are triplets with $J_{(C-D)}$ = 14 Hz. IR: the stretch at 3030–3083 in **1** changes to an sp^2-C–D stretching at 2356. A small peak at 3073 cm^{-1} corresponds to the phenylene group.

‡ Simulations were performed at 75 MHz with exchange between signals at 128.5 and 132.3 ppm assuming a Gaussian lineshape. A static line width of *ca.* 115 Hz was estimated from measurements carried out at the lowest temperature.

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