

# Solid triphenylmethanol: A molecular material that undergoes multiple internal reorientational processes on different timescales

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## Abstract

In solid triphenylmethanol, the molecules are arranged in hydrogen-bonded tetramers, and it is already well established that the hydrogen bonding in this material undergoes a dynamic switching process between different hydrogen bonding arrangements. In addition to this motion, we show here, from solid-state <sup>2</sup>H NMR studies of the deuterated material (C<sub>6</sub>D<sub>5</sub>)<sub>3</sub>COH, that each phenyl ring in this material undergoes a 180°-jump reorientation about the C<sub>6</sub>D<sub>5</sub>-C(OH) bond, with an activation energy of ca. 50 kJ mol<sup>-1</sup>. The timescale for the phenyl ring dynamics is several orders of magnitude longer than the timescale for the hydrogen bond dynamics in this material, and is uncorrelated with the dynamics of the hydrogen bonding arrangement.

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In the crystal structure of triphenylmethanol (Ph<sub>3</sub>COH; denoted TPM) [1,2], the molecules form hydrogen-bonded tetramers (Fig. 1) with the oxygen atoms positioned *approximately* at the corners of a tetrahedron. Three of the molecules (denoted “basal”) in the tetramer are related to each other by a 3-fold rotation axis and the fourth molecule (denoted “apical”) lies on this axis. Thus, the oxygen atoms from the four molecules in the tetramer form a pyramidal O<sub>4</sub> arrangement with an equilateral triangular base. The O⋯O distances (ca. 2.9 Å) within the tetramer are consistent with the tetramer being held together by O–H⋯O hydrogen bonds. Although the hydrogen atoms of the hydroxyl groups were not located in the structure determination from single-crystal X-ray diffraction data (suggestive of possible disorder of the hydrogen bonding arrangement), subsequent single-crystal neutron diffraction studies [2] confirmed that the hydrogen bonding arrangement in this material is indeed disordered (each hydroxyl hydrogen atom is disordered between different sites with

fractional occupancies, each corresponding to the formation of an O–H⋯O hydrogen bond along a different O⋯O edge of the O<sub>4</sub> pyramid).

To assess the dynamic properties of the hydrogen bonding arrangement in TPM, solid-state <sup>2</sup>H NMR studies were carried out [3] on the selectively deuterated material (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>COD; the results confirmed that the disorder in the hydrogen bonding arrangement is indeed dynamic. In the dynamic model established from these studies, the deuteron of the apical molecule undergoes a 3-site 120°-jump motion by rotation about the C–O bond (with equal populations of the three sites), whereas the deuteron of each basal molecule undergoes a 2-site 120°-jump motion by rotation about the C–O bond. The motion of the basal deuterons can be interpreted in terms of “switching” between two different hydrogen bonding arrangements (“clockwise” and “anticlockwise”) on the basal plane of the O<sub>4</sub> pyramid (involving correlated 2-site 120°-jumps of the three deuterons).

In the light of the fact that the hydrogen bonding arrangement in TPM is dynamic, it is interesting to consider whether any other aspects of this material are

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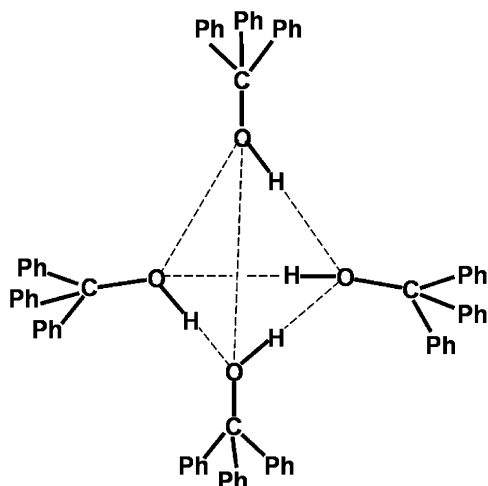


Fig. 1. Schematic representation of the tetramer in the crystal structure of triphenylmethanol ( $\text{Ph}_3\text{COH}$ ). The hydrogen bonding arrangement shown is only one of several plausible hydrogen bonding arrangements for the tetramer.

dynamic, and to assess whether other dynamic processes are correlated to the dynamics of the hydrogen bonding arrangement. In this regard, we have investigated the dynamic properties of the phenyl rings in TPM via solid-state  $^2\text{H}$  NMR studies of the deuterated material ( $\text{C}_6\text{D}_5$ ) $_3\text{COH}$  (TPM- $\text{d}_{15}$ ). Solid-state  $^2\text{H}$  NMR spectroscopy is a powerful technique for investigating molecular motion in solids [4–12]. When the rate of motion is in the range  $10^3$ – $10^8$   $\text{s}^{-1}$  (the intermediate motion regime), analysis of the  $^2\text{H}$  NMR lineshape provides detailed information on the rate, geometry and mechanism of the motion. For rates faster than  $10^8$   $\text{s}^{-1}$  (the rapid motion regime), the actual rate of motion cannot be established from  $^2\text{H}$  NMR lineshape analysis, but information on the geometry and mechanism of the motion can nevertheless be obtained. For rates slower than  $10^3$   $\text{s}^{-1}$  (the static/slow motion regime), the  $^2\text{H}$  NMR lineshape is insensitive to the occurrence of the motion.

The deuterated material TPM- $\text{d}_{15}$  was prepared by reaction of benzophenone- $\text{d}_{10}$  with  $\text{C}_6\text{D}_5\text{MgBr}$  in diethyl ether solution, followed by quenching with dilute aqueous acid, and recrystallisation of the solid product from benzene. Solid-state  $^2\text{H}$  NMR spectra were recorded for a polycrystalline sample of TPM- $\text{d}_{15}$  in the temperature range 253–423 K using a single-resonance static 5-mm probe on a Chemagnetics CMX-Infinity 300 spectrometer operating at 46.080 MHz. The conventional quadrupole echo  $\{(90^\circ)_\phi - \tau - (90^\circ)_{\phi \pm \pi/2} - \tau' - \text{acquire} - \text{recycle}\}$  pulse sequence [13] was used, with  $90^\circ$  pulse duration  $2 \mu\text{s}$ , echo delay  $\tau = 50 \mu\text{s}$ , and an eight-step phase cycle. The recycle delay ranged from 10 to 20 s depending on temperature. Simulated  $^2\text{H}$  NMR lineshapes were calculated using the MXQET program [14].

At 253 K, the  $^2\text{H}$  NMR lineshape is a classical static Pake powder pattern [10,15], characteristic of deuterons in the static/slow motion regime. Thus, any motion of the

deuterons at this temperature occurs at a rate less than ca.  $10^3$   $\text{s}^{-1}$ . From fitting this spectrum (using the program dmfit [16]), the static quadrupole coupling constant ( $\chi = e^2qQ/h$ ) and static asymmetry parameter ( $\eta$ ) were determined to be 180 kHz and 0.022, respectively. Solid-state  $^2\text{H}$  NMR spectra recorded for TPM- $\text{d}_{15}$  in the temperature range 303–423 K are shown in Fig. 2. At 303 K and higher temperatures, the  $^2\text{H}$  NMR lineshape differs from a static powder pattern, indicating that motion of the deuterons has entered the intermediate motion regime, and the fact that the  $^2\text{H}$  NMR lineshape changes as a function of temperature throughout this temperature range demonstrates that the deuterons in the phenyl rings are dynamic on the  $^2\text{H}$  NMR timescale. The observed changes in the  $^2\text{H}$  NMR lineshape are characteristic of a  $180^\circ$ -jump motion of phenyl rings about an axis passing through the C– $\text{C}_6\text{D}_5$  bond (Fig. 3). In the  $\text{C}_6\text{D}_5$  ring, four deuterons (in *ortho* and *meta* positions; denoted type A) have the same

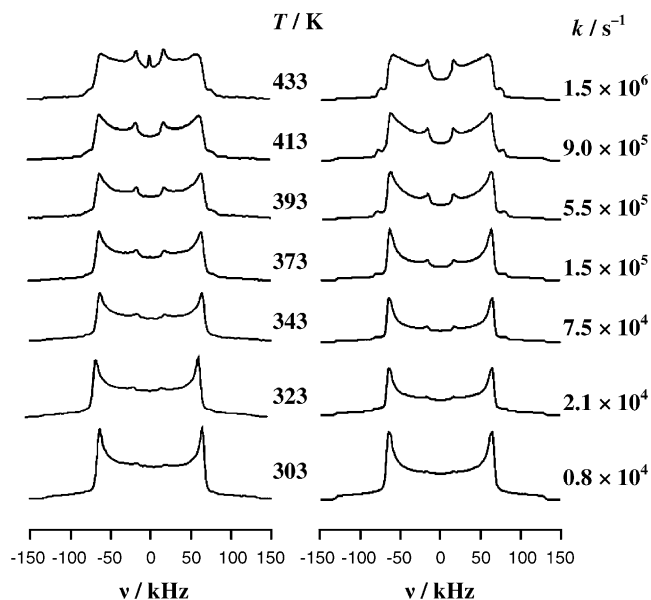


Fig. 2. Left side: experimental  $^2\text{H}$  NMR spectra recorded for TPM- $\text{d}_{15}$  as a function of temperature. Right side: the best-fit simulated  $^2\text{H}$  NMR spectrum for each experimental spectrum, with the frequency ( $k$ ) of the  $180^\circ$ -jump motion indicated.

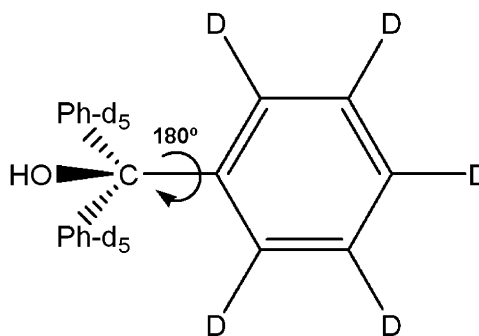


Fig. 3. Schematic illustration of the  $180^\circ$ -jump motion of the phenyl rings in TPM- $\text{d}_{15}$ .

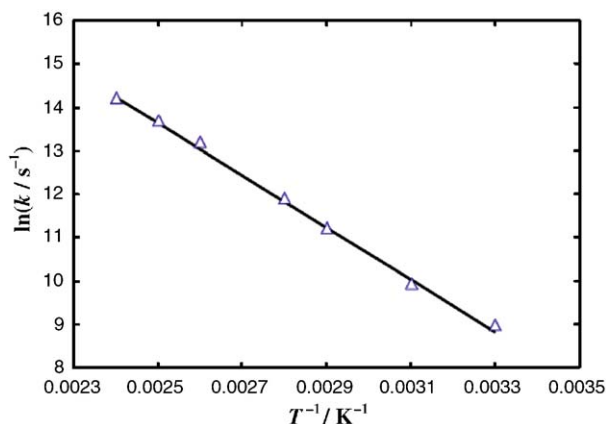


Fig. 4. Graph of  $\ln(k/s^{-1})$  versus  $T^{-1}/K^{-1}$  for the  $180^\circ$ -jump motion of the phenyl rings in TPM- $d_{15}$ .

geometric relationship to the rotation axis (with an angle of  $60^\circ$ , for idealised geometry, between the C–D bond and the rotation axis) whereas the other deuteron (*para* position; denoted type B) has a different geometric relationship to this axis (with the C–D bond collinear with the rotation axis). Thus, for this motion, the  $^2H$  NMR lineshape should comprise separate contributions from deuterons of types A and B in a 4:1 ratio. As the C–D bond for the deuteron of type B is collinear with the rotation axis, the  $^2H$  NMR lineshape for this deuteron should be the same as that of a static deuteron, irrespective of the rate of the  $180^\circ$ -jump motion of the phenyl ring about this axis. Indeed, it is clear from Fig. 2 that, at all temperatures, one component of the  $^2H$  NMR spectrum (attributed to the *para* deuteron) is a static Pake powder pattern, implying that no whole-molecule reorientation (e.g.  $120^\circ$  jumps of the whole molecule about the C–O bond direction) occurs on the  $^2H$  NMR timescale (i.e. on a timescale shorter than  $10^{-3}$  s) in this material within the temperature range studied.

Simulated  $^2H$  NMR lineshapes were calculated on the basis of the  $180^\circ$ -jump model described above for different values of the jump frequency ( $\kappa$ ), and with the values of  $\chi$  and  $\eta$  allowed to vary slightly as a function of temperature to subsume the effects of any rapid small-amplitude motions (e.g. small-angle librational motions) at these temperatures. Simulations were also carried out for slightly different values of the angle ( $\theta$ ) between the C–D bond and the rotation axis for the deuterons in the *ortho* and *meta* positions (to allow for slight distortion of the phenyl rings from ideal geometry), with the best fits to the experimental spectra obtained for  $\theta = 60^\circ$ .

The best-fit simulated spectrum at each temperature is shown in Fig. 2, from which the jump frequency  $\kappa$  is determined as a function of temperature. The temperature dependence of  $\kappa$  is found (Fig. 4) to exhibit Arrhenius behaviour (i.e.  $\kappa = A \exp(-E_a/RT)$ ), with the activation parameters estimated to be  $E_a = (49.9 \pm 1.3) \text{ kJ mol}^{-1}$  and  $\ln(A/s^{-1}) = 28.7 \pm 0.4$ .

In the temperature range studied, the rate of the  $180^\circ$ -jump motion of the phenyl rings in TPM is several orders

of magnitude slower than the dynamics of the hydrogen bonding in this material [3]. Thus, the hydrogen bond dynamics is already in the rapid motion regime (timescale shorter than ca.  $10^{-8}$  s) at 293 K, whereas the phenyl ring dynamics is still in the slow/static motion regime at this temperature (timescale longer than ca.  $10^{-3}$  s). Thus, the timescales for the hydrogen bond dynamics and the phenyl ring dynamics differ by at least five orders of magnitude, and it is clear that the dynamics of the hydrogen bonding arrangement and the dynamics of the phenyl rings are not correlated to one another. We note that the  $180^\circ$ -jump motion of each phenyl ring interconverts two orientations that are indistinguishable by diffraction techniques, and thus the structures determined from single-crystal X-ray diffraction [1] and single-crystal neutron diffraction [2] provide no hint for disorder with respect to the orientations of the phenyl rings (unlike the situation for the disorder in the hydrogen bonding arrangement, which is suggested from the single-crystal X-ray diffraction data and proven by the single-crystal neutron diffraction data). Finally, we note that the  $^2H$  NMR technique probes the dynamic properties of individual deuterons, and does not provide any insights on whether the  $180^\circ$  jumps of the three phenyl rings in a given molecule occur in a concerted fashion or whether they are independent of one another. The application of appropriate computational techniques should be able to provide valuable information on this issue.

The activation energy for the  $180^\circ$ -jump motion of the phenyl rings in TPM is similar to those for phenyl ring flips in other crystalline materials, including bacteriorhodopsin ( $50.2 \text{ kJ mol}^{-1}$ ) [17], Leu<sup>5</sup>-enkephalin (phenyl ring in the phenylalanine residue;  $37.5 \text{ kJ mol}^{-1}$ ) [18], the *p*-fluorophenyl ring in *p*-fluoro-D,L-phenylalanine ( $47.3 \text{ kJ mol}^{-1}$  above 373 K) [19] and the *p*-chlorophenyl ring in bis(*p*-chlorophenyl) sulfone ( $71 \text{ kJ mol}^{-1}$ ) [20]. The dynamics of phenyl side-groups in polymers (for which it can be necessary to invoke a distribution of rates of motion) have also been studied; the activation energies for  $180^\circ$  jumps of phenyl rings in such systems are often somewhat lower (e.g.  $28 \text{ kJ mol}^{-1}$  for poly(L-phenylalanine) [21]) than those reported above for crystalline molecular materials.

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