

Unravelling the Disordered Hydrogen Bonding Arrangement in Solid Triphenylmethanol

Heliodoro Serrano-González,[†] Kenneth D M Harris,^{*,†} Chick C Wilson,[‡] Abil E Aliev,[§] Simon J Kitchin,[†] Benson M Kariuki,[†] Marta Bach-Vergés,[†] Christopher Glidewell,^{||} Elizabeth J MacLean,[§] and Winnie W Kagunya[‡]

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K., ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, U.K., Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., and School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

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In the crystal structure of triphenylmethanol (Ph_3COH), the molecules form hydrogen-bonded tetramers, with the oxygen atoms positioned approximately at the corners of a tetrahedron. In the average crystal structure, three of the Ph_3COH molecules (denoted as “basal”) in the tetramer are related to each other by a 3-fold rotation axis and the fourth molecule (denoted as “apical”) lies on this axis. Previously, the dynamic properties of the hydrogen-bonding arrangement have been probed through solid-state ^2H NMR spectroscopic investigations of Ph_3COD . There are two dynamically distinguishable types of hydroxyl hydrogen atoms (deuterons), denoted d^1 and d^3 , with relative populations in the ratio 1:3. Each d^1 deuteron undergoes three-site 120° jumps by rotation about the C–OD bond, with equal populations of the three sites involved in this motion. Each d^3 deuteron undergoes two-site 120° jumps by rotation about the C–OD bond, with equal populations of the two sites involved in this motion. In the present paper, we focus on structural characterization of the hydrogen-bonding arrangement in solid triphenylmethanol. Single-crystal neutron diffraction has been used to determine accurate positions of the hydroxyl hydrogen atoms in the hydrogen-bonding arrangement, single-crystal X-ray diffraction has extended previous structural studies across a wider temperature range, and high-resolution solid-state ^{13}C NMR spectroscopy has provided insights into local structural aspects of the hydrogen-bonded tetramers. Importantly, the neutron diffraction results show that, for both the apical and basal molecules in the average crystal structure, the hydroxyl hydrogen atoms are disordered among three sites, corresponding closely to the geometries expected for $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds. The populations of the three hydroxyl hydrogen sites for each molecule are statistically equal, and there is thus an apparent dilemma in bringing together information on the spatial distribution of the hydroxyl hydrogens conveyed by the average crystal structure and information on the spatial distribution of the hydroxyl hydrogens implicated by the dynamic model determined from ^2H NMR spectroscopy. Through a detailed discussion of the different ways in which structural information is averaged in the different techniques (neutron diffraction, X-ray diffraction, ^2H NMR, and ^{13}C NMR) that have been applied in our studies of solid triphenylmethanol, these apparent difficulties can be completely reconciled. In conclusion, we present a coherent description of the structural and dynamic properties of the hydrogen-bonding arrangement in solid triphenylmethanol, which is consistent with the information provided by each of the techniques used.

1. Introduction

The crystal structure of triphenylmethanol (Ph_3COH), determined at ambient temperature from single-crystal X-ray diffraction data¹ comprises hydrogen-bonded tetramers of triphenylmethanol molecules (Figure 1a). The space group is $R\bar{3}$, and in each tetramer one molecule lies on a 3-fold symmetry axis whereas the other three molecules are related to each other by rotation about this axis. Subsequently, the crystallographically unique molecule in the tetramer (in the average crystal structure) is referred to as “apical” and the other three molecules are referred to as “basal” (see Figure 1b). Although the molecular packing arrangement in the average crystal structure gives rise to $R\bar{3}$ space group and thus C_3 point symmetry for the tetramer, the tetramer actually approximates to tetrahedral symmetry with the C–O bonds lying along the 3-fold axes of the approximate tetrahedron. As a reflection of the approximate tetrahedral symmetry of the O_4 core of the tetramer, the $\text{O}_{\text{basal}} \cdots \text{O}_{\text{basal}}$ and

$\text{O}_{\text{basal}} \cdots \text{O}_{\text{apical}}$ distances [2.884(10) and 2.896(12) Å, respectively] in the structure determined previously¹ are equal within the precision of the experimental measurements. Thus, in the average crystal structure, the hydroxyl groups of the apical and basal molecules have essentially identical local environments.

In the previous determination of the crystal structure from single-crystal X-ray diffraction data at ambient temperature,¹ the hydrogen atoms of the hydroxyl groups were not located. However, the $\text{O} \cdots \text{O}$ distances suggest that the tetramer is held together by $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds (this suggestion is supported by the results of computational studies² of a model system comprising a hydrogen-bonded tetramer of methanol molecules). If the hydrogen atoms involved in the hydrogen bonding in triphenylmethanol are indeed located along (or close to) the $\text{O} \cdots \text{O}$ edges (rather than the faces) of the O_4 unit of the tetramer (thereby forming the shortest $\text{O} \cdots \text{H} \cdots \text{O}$ distances and presumably the strongest hydrogen bonds), the fact that there are four $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds distributed among six $\text{O} \cdots \text{O}$ edges suggests that the hydrogen-bonding arrangement may be disordered.

Solid-state ^2H NMR spectroscopy of the deuterated material

* To whom correspondence should be addressed

[†] University of Birmingham.

[‡] Rutherford Appleton Laboratory.

[§] University College London.

^{||} University of St. Andrews.

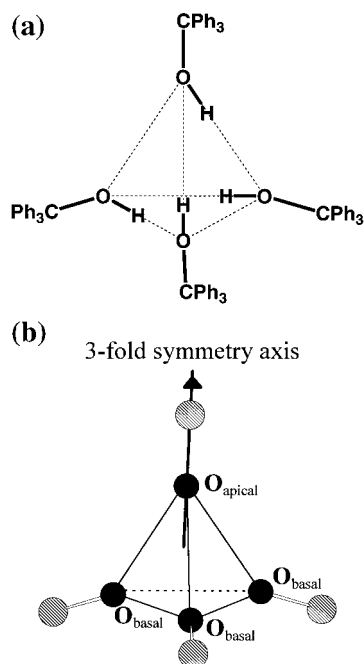


Figure 1. (a) Schematic representation of the tetramer in the crystal structure of triphenylmethanol (Ph_3COH). The hydrogen-bonding arrangement shown is only one of several plausible hydrogen-bonding arrangements for the tetramer. (b) Oxygen atoms and the carbon atoms bonded to oxygen in the tetramer. Note the approximate tetrahedral symmetry of this unit.

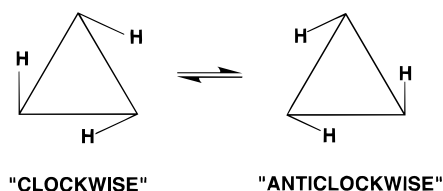


Figure 2. Illustration of the dynamic behavior of the hydrogen-bonding arrangement involving the three d^3 sites in the tetramer.

Ph_3COD has confirmed³ that there is dynamic disorder on the ^2H NMR time scale (10^{-3} – 10^{-8} s) over the temperature range (97–373 K) studied and has elucidated the mechanism of the motion of the deuterons of the (deuterated) hydroxyl groups. This mechanism involves two dynamically distinguishable types of deuterons, denoted the “ d^1 ” and “ d^3 ” deuterons, with relative populations in the ratio 1:3, respectively. Each d^1 deuteron undergoes three-site 120° jumps by rotation about the C–OD bond, with equal populations of the three sites involved in this motion. Each d^3 deuteron undergoes two-site 120° jumps by rotation about the C–OD bond, with equal populations of the two sites involved in this motion. In addition, each type of deuteron undergoes rapid libration (by reorientation about the C–OD bond) with the libration amplitude increasing as temperature is increased. It is reasonable to propose that, in each tetramer, the hydroxyl group of one molecule undergoes motion of type d^1 and the hydroxyl groups of the other three molecules undergo motion of type d^3 . The behavior of the d^3 molecules can be interpreted in terms of two different hydrogen-bonding arrangements (“clockwise” and “anticlockwise”, as shown in Figure 2) on the plane of the O_4 unit containing the oxygen atoms of the three d^3 molecules. The two-site 120° jump motion of the hydroxyl groups of the d^3 molecules interconverts between these two hydrogen-bonding arrangements and clearly invokes correlated jumps of the hydroxyl groups of all three molecules. The temperature dependences of the jump frequencies for the deuterons of types d^1 and d^3 are described well by Arrhenius

behavior, and the activation energies are estimated³ to be 10 and 21 kJ mol^{-1} , respectively.

In this dynamic model, there are three deuteron sites for the d^1 molecule, with each site having an average occupancy of $1/3$, and there are two deuteron sites for each d^3 molecule, with each site having an average occupancy of $1/2$. These sites are all interpreted in terms of $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonding along the $\text{O}\cdots\text{O}$ edges of the O_4 unit of the tetramer. The previous X-ray diffraction study¹ did not locate the hydrogen atoms of the hydroxyl groups, and the above discussion has been based on assigning a structural interpretation to the dynamic model in the knowledge that the $\text{O}\cdots\text{O}$ distances are consistent with $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonding. Nevertheless, it is important to establish the actual spatial distribution of the hydroxyl hydrogens in this structure, and with this aim we report here the results of neutron diffraction studies of solid triphenylmethanol.

Although it may be tempting to equate the d^1 site of the dynamic model with the apical molecule in the average crystal structure and to equate the d^3 sites of the dynamic model with the basal molecules in the average crystal structure, it is important to stress that the ^2H NMR data analysis does not require that the d^1 site in each tetramer corresponds to the apical molecule and that the d^3 sites in each tetramer correspond to the basal molecules. We return to discuss this point in detail in section 4.

In addition to the disorder in the hydrogen bonding described above, another aspect of disorder in the crystal structure of triphenylmethanol concerns the existence of two different orientations of the tetramers within the crystal. In the structure at ambient temperature reported previously,¹ the ratio of the two different tetramer orientations is 71:29 (as discussed below, this ratio has been found to differ slightly from one crystal to another). We refer to these different orientations as the major and minor tetramers. The structures of the major and minor tetramers are essentially identical,¹ and it is justified to assume that the structural and dynamic properties of the hydrogen-bonding arrangements in the major and minor tetramers should be essentially identical. Furthermore, as the hydrogen-bonding arrangement at the core of each tetramer is essentially “isolated” from the surrounding environment, the structural and dynamic properties of the hydrogen-bonding arrangement should not be influenced significantly by the overall orientation of the tetramer within the crystal. This fact is reflected by the essentially identical geometries of the O_4 units in the major and minor tetramers. There is no evidence from any of our experimental studies to suggest that there are any detectable differences between the hydrogen-bonding arrangements in the major and minor tetramers.

In this paper, we focus on structural characterization of the hydrogen-bonding arrangement in triphenylmethanol using single-crystal neutron diffraction, single-crystal X-ray diffraction, and high-resolution solid-state ^{13}C NMR spectroscopy. The single-crystal neutron diffraction experiments have led to an accurate determination of the positions of the hydrogen atoms in the hydrogen-bonding arrangement, the single-crystal X-ray diffraction experiments have extended previous studies¹ across a wider temperature range, and the high-resolution solid-state ^{13}C NMR experiments have provided insights into local structural aspects of the hydrogen-bonded tetramers.

2. Experimental Section

Crystals of triphenylmethanol were grown at ambient temperature by slow evaporation of solvent from a saturated solution containing triphenylmethanol in benzene. A large single crystal

TABLE 1: Crystal Data and Structure Refinement Parameters for the Neutron and X-ray Diffraction Data

radiation type	neutron	X-ray	X-ray
temperature	(100 ± 1) K	(293 ± 2) K	(113 ± 2) K
diffractometer type	SXD neutron TOF Laue diffractometer	Rigaku R-Axis II	Rigaku R-Axis II
detectors	64 × 64, 3 mm pixel scintillator PSDs	image plate 200 × 200 mm ²	image plate 200 × 200 mm ²
wavelength range	0.48–4.8 Å	0.71069 Å	0.71069 Å
space group	R3	R3	R3
unit cell dimensions	<i>a</i> = 19.089(6) Å <i>c</i> = 26.776(9) Å	<i>a</i> = 19.311(1) Å <i>c</i> = 26.875(1) Å	<i>a</i> = 19.107(1) Å <i>c</i> = 26.800(1) Å
cell volume	8450(5) Å ³	8679.5(7) Å ³	8473.1(8) Å ³
<i>Z</i>	24	24	24
θ range for data collection	1.10°–9.90°	1.42°–25.53°	1.45°–25.40°
index ranges for reflections	–16 ≤ <i>h</i> ≤ 16 –17 ≤ <i>k</i> ≤ 17 –31 ≤ <i>l</i> ≤ 28	–22 ≤ <i>h</i> ≤ 22 –23 ≤ <i>k</i> ≤ 23 –32 ≤ <i>l</i> ≤ 32	–22 ≤ <i>h</i> ≤ 23 –21 ≤ <i>k</i> ≤ 22 –31 ≤ <i>l</i> ≤ 32
reflections collected	9485	14846	14502
independent reflections	1082 (<i>R</i> _{int} = 0.075)	3448 (<i>R</i> _{int} = 0.046)	3313 (<i>R</i> _{int} = 0.066)
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
restraints in refinement	115	1	1
refined parameters	428	322	322
goodness-of-fit on <i>F</i> ²	1.272	1.275	1.216
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> (<i>F</i>) = 0.098 w <i>R</i> (<i>F</i> ²) = 0.259	<i>R</i> (<i>F</i>) = 0.114 w <i>R</i> (<i>F</i> ²) = 0.226	<i>R</i> (<i>F</i>) = 0.116 w <i>R</i> (<i>F</i> ²) = 0.235
<i>R</i> indices (all data)	<i>R</i> (<i>F</i>) = 0.098 w <i>R</i> (<i>F</i> ²) = 0.259	<i>R</i> (<i>F</i>) = 0.117 w <i>R</i> (<i>F</i> ²) = 0.228	<i>R</i> (<i>F</i>) = 0.123 w <i>R</i> (<i>F</i> ²) = 0.236
largest difference map peak	0.75 fm Å ^{–3}	0.129 e Å ^{–3}	0.251 e Å ^{–3}
largest difference map hole	–0.74 fm Å ^{–3}	–0.117 e Å ^{–3}	–0.172 e Å ^{–3}

(dimensions 3 × 3 × 2.5 mm³) was used for neutron diffraction. Subsequently, a piece of this crystal was cut and used for single-crystal X-ray diffraction.

Single-crystal neutron diffraction experiments were carried out on the SXD instrument at the ISIS facility (neutron spallation source) using the time-of-flight Laue diffraction method.^{4,5} This method uses a wavelength-sorted white neutron beam, along with large-area position-sensitive detectors, to allow a large volume of reciprocal space to be measured for a given crystal setting (a “frame”). The crystal was mounted on a Displex closed-cycle refrigerator inside a (χ, φ) orienter, and the temperature was held at (100 ± 1) K throughout the experiment. The full data collection comprised a series of such frames, each collected with a stationary crystal-detector arrangement. The data collection parameters are summarized in Table 1. A total of 42 frames were collected, each containing information from two detectors, with a typical exposure time of 6 h per frame. The intensities were extracted and reduced to structure factors using standard SXD procedures.⁵ Structure refinement from the neutron diffraction data (comprising 1082 unique merged reflections) was carried out using the program SHELXL-97.⁶

Single-crystal X-ray diffraction experiments were carried out at (293 ± 2) K and (113 ± 2) K using Mo K α radiation on a Rigaku R-Axis II diffractometer equipped with an image plate detector. A standard MSC low-temperature device was used for experiments below ambient temperature. The data collection at 293 K comprised 45 frames, each recorded over an oscillation range of 4° with an exposure time of 25 min/frame and a crystal-to-detector distance of 80 mm. The data collection at 113 K differed only in the exposure time (20 min/frame). The data collection parameters at 293 and 113 K are reported in Table 1. Structure refinement from the X-ray diffraction data was carried out using the program SHELXL-93.⁷

High-resolution solid-state ¹³C NMR spectra were recorded for a polycrystalline sample of triphenylmethanol enriched with ¹³C in the carbon bonded to oxygen (Ph₃¹³COH), allowing increased sensitivity in comparison to samples with natural isotopic abundances. The ¹³C NMR spectra were recorded (direct polarization using a single ¹³C 90° pulse) at 75.4 MHz on a Chemagnetics CMX-Infinity 300 spectrometer, with magic angle

sample spinning and high-power ¹H decoupling. The TPPM decoupling sequence⁸ (with 170° decoupling pulses and a 15° phase alternation) was used. A Chemagnetics 4 mm MAS probe was used, with spinning frequency (4000 ± 2) Hz and ¹H decoupler field strength of ca. 62.5 kHz. Chemical shifts are reported relative to tetramethylsilane. The recycle delay was 30 s. A similar series of experiments was carried out on a Bruker MSL300 spectrometer over the same temperature range and with similar spectrometer conditions. There were no significant differences between the results of the experiments carried out on the different spectrometers.

3. Results and Discussion

3.1. Neutron Diffraction. Neutron diffraction is particularly suitable for locating hydrogen atoms in solids, as the magnitude of the neutron scattering length for hydrogen (–0.374 × 10^{–12} cm) is comparable to the neutron scattering lengths for carbon (0.665 × 10^{–12} cm) and oxygen (0.580 × 10^{–12} cm). In contrast, the X-ray scattering power of an atom is proportional to its atomic number, limiting the ability to locate hydrogen atoms reliably from X-ray diffraction data. Furthermore, the disorder of the hydrogen-bonding arrangement in triphenylmethanol (which leads to hydrogen positions with fractional occupancies in the average crystal structure) makes it even more difficult to determine the average positions of the hydroxyl hydrogen atoms from X-ray diffraction data.

Our previous low-temperature powder X-ray diffraction studies³ have shown that there is no change in the crystal structure (no phase transitions) in the temperature range from 293 to 128 K. Thus, the fractional atomic coordinates in the crystal structure reported previously¹ (for all atoms except the hydroxyl hydrogen atoms) at ambient temperature were used as the starting point for structure refinement calculations using the neutron diffraction data recorded at 100 K. We recall that the asymmetric unit comprises one basal molecule and one-third of the apical molecule in the tetramer. As the number of independent reflections is comparatively low, the refinement calculations were subjected to appropriate constraints and/or restraints to limit the number of refined parameters. For both the major and minor tetramers, the benzene rings were

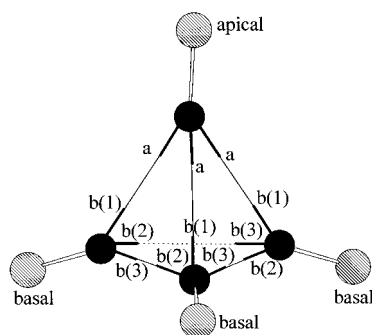


Figure 3. Description of the constraints imposed by the symmetry of the crystal structure on the populations (denoted P) of sites occupied by the hydroxyl hydrogen atoms in the average crystal structure (assuming that O—H···O hydrogen bonds are formed). Note: $P_a = 1/3$; $P_{b(1)} + P_{b(2)} + P_{b(3)} = 1$ [with no other restrictions on the relative values of $P_{b(1)}$, $P_{b(2)}$, and $P_{b(3)}$].

constrained to be perfect hexagons, the position of each phenyl hydrogen atom was restrained to lie on the bisector of the C—C_H—C angle (where C_H denotes the atom bonded to the hydrogen and C denotes the ring carbon atoms bonded to C_H) and to lie in the plane of the phenyl ring. Each H—C distance was restrained according to the standard value for H—C(phenyl) bonds.⁹ For the major tetramer, anisotropic displacement parameters were ultimately refined for all carbon atoms, all oxygen atoms, and all hydrogen atoms of the phenyl rings. For the minor tetramer, isotropic displacement parameters were refined for all atoms, with all phenyl hydrogen atoms constrained to have the same value and all carbon atoms of a given phenyl ring constrained to have the same value.

After refinement under the above conditions, the main features in the difference Fourier map could be interpreted as positions of hydroxyl hydrogen atoms in the major tetramer (the neutron scattering cross section for hydrogen is negative, and missing hydrogen atoms appear in the difference Fourier map as holes rather than peaks). The hole representing the hydroxyl hydrogen of the apical molecule had a depth of $-0.87 \text{ fm } \text{\AA}^{-3}$ (O—H distance of 0.92 \AA ; C—O—H angle of 123.3°). The three holes representing the hydroxyl hydrogen sites for the basal molecule in the asymmetric unit had depths of -0.74 , -0.58 , and $-0.49 \text{ fm } \text{\AA}^{-3}$ (O—H distances of 0.96 , 0.93 , 0.99 \AA , respectively; C—O—H angles of 118.3° , 125.8° , 92.3° , respectively). We note that the space group imposes restrictions on the occupancies of the sites occupied by the hydroxyl hydrogens in the average crystal structure. Thus, the 3-fold axis lying along the C—O bond of the apical molecule requires that the hydroxyl hydrogen of this molecule must be disordered; if it is disordered among three sites, the occupancy of each site must be $1/3$ (see Figure 3). For a given basal molecule, there are no such symmetry restrictions concerning the average distribution of the hydroxyl hydrogens; however, the 3-fold axis dictates that the hydroxyl hydrogen of each basal molecule must have the same spatial distribution (see Figure 3).

Subsequent refinement calculations adopted the following strategy. The occupancy of the hydroxyl hydrogen of the apical molecule was fixed at $1/3$ of the occupancy of the molecule, and the occupancies of the three (crystallographically independent) hydroxyl hydrogens of the basal molecule in the asymmetric unit were restrained such that their sum was equal to the occupancy of the molecule. A common isotropic displacement parameter was refined for these hydrogen atoms. The O—H distances were restrained to the standard value,⁹ all H···H distances between different sites for a given hydroxyl hydrogen were restrained to be equal, and all C—O—H angles were

TABLE 2: Final Refined Fractional Coordinates, Occupancies, and Isotropic Displacement Parameters of the Hydroxyl Hydrogen Atoms of the Major Tetramer of Triphenylmethanol (H1A Is in the Apical Molecule, and H2A, H3A, and H4A Are in the Basal Molecule)^a

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/\text{\AA}^2$	occupancy
H(1A)	−0.049(3)	−0.005(6)	0.3061(16)	0.072(14)	1/3
H(2A)	−0.074(3)	−0.059(3)	0.217(2)	0.072(14)	0.35(5)
H(3A)	−0.099(3)	−0.039(4)	0.2670(7)	0.072(14)	0.31(5)
H(4A)	−0.062(2)	0.0257(16)	0.226(2)	0.072(14)	0.34(1)

^a The occupancies of the hydroxyl hydrogen sites are given relative to the occupancy of the molecule.

restrained to be equal. Attempts to remove these constraints/restraints in the refinement led to implausible geometric features. At this stage, the refined occupancies of the three sites for the hydroxyl hydrogen of the basal molecule in the major tetramer were $0.35(5)$, $0.34(1)$, and $0.31(5)$. Within the precision of the experimental measurements, the populations of these sites are indistinguishable.

The hydroxyl hydrogens of the minor tetramer could not be located from the difference Fourier map, and these hydrogen atoms were inserted in calculated positions based on those determined above for the major tetramer. The isotropic displacement parameters were constrained to be the same as those for the hydroxyl hydrogens of the major tetramer, and the occupancies of the three hydroxyl hydrogen sites for the basal molecule were constrained to be equal (as suggested by the results for the major tetramer). The hydroxyl hydrogens of the minor tetramer were restrained to have the same O—H distances as the major tetramer.

The final refinement parameters are given in Table 1. The final refined coordinates, occupancies, and isotropic displacement parameters for the hydroxyl hydrogens of the major tetramer are given in Table 2. The structure of the hydrogen-bonded core of the tetramer is shown in Figure 4, viewed along the C—O bonds of the apical and basal molecules [parts a and b of Figure 4, respectively]. The closest intermolecular H···O distances are $2.16(4)$, $2.13(4)$, $2.18(4)$, and $2.16(4) \text{ \AA}$ for H1A, H2A, H3A, and H4A, respectively, the O—H···O angles are $133(4)^\circ$, $135(4)^\circ$, $131(4)^\circ$, and $133(4)^\circ$ for H1A, H2A, H3A, and H4A, respectively, and the C—O—H angle (refined as a common value) is $113(3)^\circ$. The final refined coordinates, occupancies, and equivalent isotropic displacement parameters of all atoms are reported in Table 3.

In summary, the neutron diffraction results show that, for both the apical and basal molecules in the average crystal structure, the hydroxyl hydrogen atoms are disordered among three sites, corresponding closely to the geometries expected for O—H···O hydrogen bonds. The populations of the three hydroxyl hydrogen sites for each molecule are statistically equal. We emphasize that the hydroxyl hydrogen atom cannot actually lie exactly along the O···O edges, as the C—O—H angle (ca. 113°) and the C—O···O angle (ca. 145°) are not equal.

3.2. X-ray Diffraction. The single-crystal X-ray diffraction data sets recorded at both 293 and 113 K are consistent with the space group and unit cell determined previously at ambient temperature.¹ The crystal structures were refined using, as the starting model, the structure (all atoms except the hydroxyl hydrogen atoms) determined previously¹ at ambient temperature. For the major tetramer, anisotropic displacement parameters were ultimately refined for all non-hydrogen atoms. For the minor tetramer, anisotropic displacement parameters were ultimately refined for the oxygen atoms and the carbon atoms bonded to oxygen, whereas isotropic displacement parameters

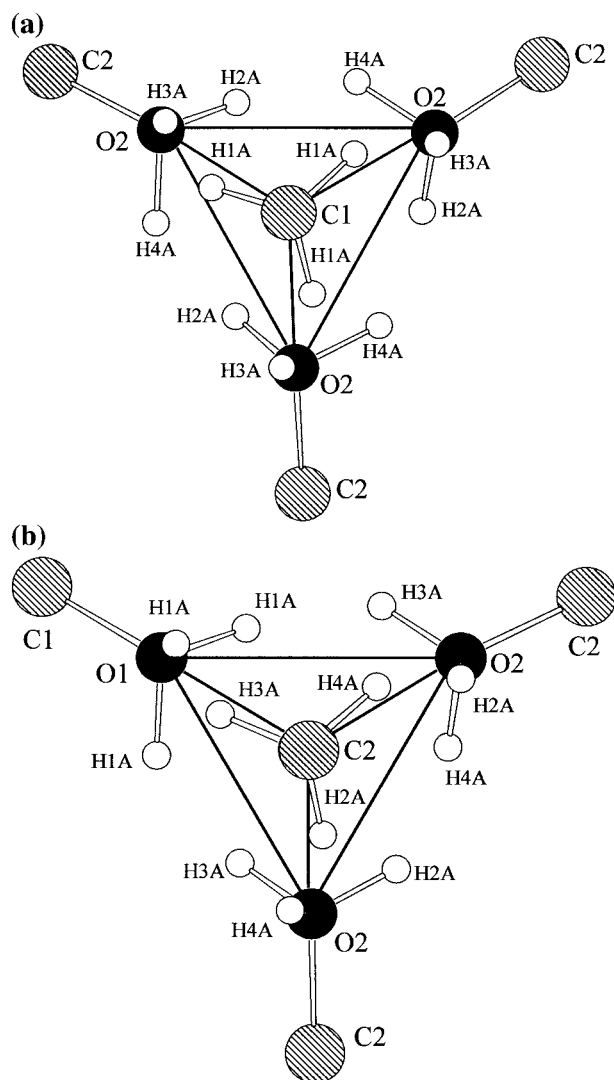


Figure 4. Central part [the (COH)₄ core] of the tetramer in the average crystal structure of triphenylmethanol determined at 100 K from neutron diffraction data, viewed (a) approximately along the C—O bond of the apical molecule (C—O1) and (b) approximately along the C—O bond of a basal molecule (C—O2). Oxygen atoms are represented by filled circles, carbon atoms by shaded circles, and hydrogen atoms by empty circles. The figure shows that the sites occupied by the hydroxyl hydrogen atoms lie approximately along the O···O edges of the tetramer and are thus interpreted in terms of O—H···O hydrogen bonding.

were refined for the carbon atoms of the phenyl rings. For the major tetramer, no restraints/constraints were imposed on the geometries of the molecules, whereas for the minor tetramer, the phenyl rings were constrained to be regular hexagons. For both major and minor tetramers, the hydrogen atoms of the phenyl rings were placed in calculated positions and were refined using a riding model.

At the last stage of refinement for the data recorded at 293 K, the first, second, and fourth highest peaks (0.13, 0.12, 0.12 e Å⁻³) in the difference Fourier map had distances of 0.75, 0.72, and 0.85 Å to the oxygen atom of the basal molecule, and C—O-peak angles of 113.6°, 112.1° and 118.9°. These peaks are interpreted as hydroxyl hydrogen sites for the basal molecule. It was not considered appropriate to refine the positions and occupancies of these sites from the X-ray diffraction data. None of the first 20 peaks of the difference Fourier map was consistent with a hydroxyl hydrogen site for the apical molecule.

At the last stage of refinement for the data recorded at 113 K, the four highest peaks (0.25, 0.24, 0.21, 0.16 e Å⁻³) in the

difference Fourier map could be interpreted as hydroxyl hydrogen sites for the basal and apical molecules. The O-peak distances are 0.81, 0.70, 0.57 (basal), and 0.66 Å (apical), and the C—O-peak angles are 99.5°, 99.3°, 97.2° (basal), and 86.3° (apical). Again, it was not considered appropriate to refine the positions and occupancies of these hydroxyl hydrogen sites.

In summary, the X-ray diffraction results are consistent with disorder of the hydroxyl hydrogen for each basal molecule over three sites, although reliable information on the relative populations of these sites cannot be obtained. The final refinement parameters for the crystal structure determined from the X-ray diffraction data at 293 and 113 K are given in Table 1. The final refined coordinates and equivalent isotropic displacement parameters are reported in Table 4.

3.3. Discussion of Structural Properties. The structure determined here from single-crystal X-ray diffraction data at 293 K does not differ significantly from the structure determined previously¹ at ambient temperature. However, the structure determined here has greater precision (lower estimated standard deviations in the refined parameters) presumably because more independent reflections were measured in this work (14 846 total, 3448 independent) than in the previous work (3916 total, 2467 independent). There are no significant differences between the crystal structures determined at 293 and 113 K, except contraction of the lattice on cooling.

The O···O distances determined for the major and minor tetramers from neutron diffraction data (100 K) and X-ray diffraction data (293 and 113 K) are reported in Table 5. The estimated standard deviations in the O···O distances determined from the X-ray diffraction data are lower than those determined from the neutron diffraction data. Our results confirm (with higher precision than the previous study¹) that the O_{basal}···O_{basal} and O_{apical}···O_{basal} distances are equal within the precision of the experimental measurements. Thus, the symmetry of the O₄ core of the tetramer is described to a good approximation by point groups *T* and *T_d*. The complete tetramer (considering also the positions and orientations of the phenyl rings) approximates closely to point symmetry *T* but does not approximate to point group *T_d*, as evident from Figure 5.

Our neutron diffraction data show that, in the average crystal structure, the hydroxyl hydrogen atom of each molecule in the tetramer is distributed among three sites with statistically equal occupancies, corresponding to O—H···O hydrogen bonds along the three “available” edges of the O₄ unit. Our X-ray diffraction data support this description, while recognizing that neutron diffraction is a significantly more reliable approach for establishing information on the location of hydrogen atoms in solids.

3.4. Solid-State NMR. To explore in more detail the local structural properties of solid triphenylmethanol, we have carried out high-resolution solid-state ¹³C NMR experiments (Figure 6) on Ph₃¹³COH in the temperature range 298–138 K. Such experiments may be able to assess whether the carbon atoms of the apical and basal molecules experience different local environments (provided the differences in isotropic chemical shifts for the different local environments are significant in comparison with the intrinsic ¹³C NMR line width for each environment). Our discussion of results for the labeled material Ph₃¹³COH focuses entirely on the ¹³C environment of the COH group.

At 298 K, the spectrum comprises one peak with a clearly discernible shoulder. The overall line shape may be fitted well (Figure 7) using two peaks with a relative intensity ratio of 3:1, a chemical shift separation of 0.20 ppm (15.1 Hz) and line

TABLE 3: Final Refined Fractional Coordinates, Equivalent Isotropic Displacement Parameters (U_{eq}), and Occupancies for the Crystal Structure of Triphenylmethanol Determined at 100 K from Single-Crystal Neutron Diffraction Data^{a,b}

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$	occupancy		<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$	occupancy
H(1A)	−0.049(3)	−0.005(6)	0.3061(16)	0.072(14)	0.2506(10)	H(2B)	−0.0223(19)	−0.088(3)	0.269(4)	0.072(14)	0.0826(10)
H(2A)	−0.074(3)	−0.059(3)	0.217(2)	0.072(14)	0.264(39)	H(3B)	−0.091(4)	−0.081(6)	0.244(3)	0.072(14)	0.0826(10)
H(3A)	−0.099(3)	−0.039(4)	0.2670(7)	0.072(14)	0.236(39)	H(4B)	−0.066(6)	−0.050(2)	0.297(3)	0.072(14)	0.0826(10)
H(4A)	−0.062(2)	0.0257(16)	0.226(2)	0.072(14)	0.252(6)	O(3)	0	0	0.1911(17)	0.06(2)	0.248(3)
O(1)	0	0	0.3200(7)	0.060(9)	0.752(3)	C(3)	0	0	0.1384(16)	0.038(15)	0.248(3)
C(1)	0	0	0.3728(6)	0.030(5)	0.752(3)	O(4)	−0.074(2)	−0.0934(16)	0.2753(16)	0.054(14)	0.248(3)
O(2)	−0.0988(8)	−0.0307(11)	0.2317(6)	0.065(6)	0.752(3)	C(4)	−0.132(2)	−0.1710(16)	0.2934(14)	0.048(11)	0.248(3)
C(2)	−0.1766(7)	−0.0553(9)	0.2122(4)	0.041(3)	0.752(3)	C(51)	−0.086(2)	−0.018(3)	0.1215(17)	0.087(10)	0.248(3)
C(11)	−0.0614(5)	−0.0861(5)	0.3919(3)	0.035(3)	0.752(3)	H(52)	−0.141(4)	−0.096(4)	0.1844(17)	0.110(11)	0.248(3)
C(12)	−0.1318(6)	−0.1303(6)	0.3643(3)	0.055(4)	0.752(3)	C(52)	−0.152(3)	−0.073(3)	0.1501(13)	0.087(10)	0.248(3)
H(12)	−0.1400(8)	−0.1063(9)	0.3299(5)	0.103(16)	0.752(3)						
C(13)	−0.1916(5)	−0.2056(5)	0.3811(5)	0.072(6)	0.752(3)	C(53)	−0.230(2)	−0.098(3)	0.1345(15)	0.087(10)	0.248(3)
H(13)	−0.2464(9)	−0.2401(8)	0.3596(7)	0.130(19)	0.752(3)	H(53)	−0.281(3)	−0.140(4)	0.157(2)	0.110(11)	0.248(3)
C(14)	−0.1810(7)	−0.2367(5)	0.4256(5)	0.072(6)	0.752(3)	C(54)	−0.2432(19)	−0.068(3)	0.0904(16)	0.087(10)	0.248(3)
H(14)	−0.2275(11)	−0.2953(8)	0.4387(7)	0.14(2)	0.752(3)	H(54)	−0.304(2)	−0.087(4)	0.078(2)	0.110(11)	0.248(3)
C(15)	−0.1106(8)	−0.1925(7)	0.4533(4)	0.052(5)	0.752(3)	C(55)	−0.178(2)	−0.013(3)	0.0617(13)	0.087(10)	0.248(3)
H(15)	−0.1024(11)	−0.2167(10)	0.4879(6)	0.104(15)	0.752(3)	H(55)	−0.188(3)	0.010(4)	0.0274(17)	0.110(11)	0.248(3)
C(16)	−0.0508(6)	−0.1172(6)	0.4364(3)	0.038(4)	0.752(3)	C(56)	−0.099(2)	0.012(3)	0.0773(16)	0.087(10)	0.248(3)
H(16)	0.0036(9)	−0.0830(10)	0.4578(5)	0.099(13)	0.752(3)	H(56)	−0.049(3)	0.054(4)	0.055(2)	0.110(11)	0.248(3)
C(21)	−0.2360(4)	−0.1413(5)	0.2310(4)	0.044(4)	0.752(3)	C(61)	−0.2188(18)	−0.196(2)	0.2742(15)	0.063(7)	0.248(3)
C(22)	−0.2096(5)	−0.1971(6)	0.2347(4)	0.057(5)	0.752(3)	C(62)	−0.2358(18)	−0.1339(16)	0.2804(13)	0.063(7)	0.248(3)
H(22)	−0.1471(8)	−0.1781(9)	0.2288(6)	0.098(13)	0.752(3)	H(62)	−0.190(2)	−0.0760(19)	0.295(2)	0.110(11)	0.248(3)
C(23)	−0.2643(8)	−0.2774(6)	0.2460(4)	0.078(7)	0.752(3)	C(63)	−0.312(2)	−0.1461(19)	0.2683(13)	0.063(7)	0.248(3)
H(23)	−0.2438(11)	−0.3205(9)	0.2488(7)	0.16(3)	0.752(3)	H(63)	−0.325(3)	−0.098(3)	0.273(2)	0.110(11)	0.248(3)
C(24)	−0.3454(7)	−0.3020(4)	0.2536(5)	0.083(7)	0.752(3)	C(64)	−0.3710(18)	−0.221(2)	0.2499(15)	0.063(7)	0.248(3)
H(24)	−0.3878(10)	−0.3644(8)	0.2624(7)	0.14(2)	0.752(3)	H(64)	−0.430(2)	−0.230(3)	0.241(2)	0.110(11)	0.248(3)
C(25)	−0.3718(4)	−0.2463(6)	0.2499(5)	0.085(7)	0.752(3)	C(65)	−0.354(2)	−0.2829(18)	0.2437(16)	0.063(7)	0.248(3)
H(25)	−0.4345(8)	−0.2654(9)	0.2558(7)	0.120(17)	0.752(3)	H(65)	−0.400(3)	−0.341(2)	0.229(2)	0.110(11)	0.248(3)
C(26)	−0.3171(5)	−0.1660(5)	0.2386(4)	0.049(4)	0.752(3)	C(66)	−0.278(2)	−0.2706(18)	0.2558(17)	0.063(7)	0.248(3)
H(26)	−0.3376(8)	−0.1228(8)	0.2358(6)	0.094(13)	0.752(3)	H(66)	−0.265(3)	−0.319(2)	0.251(3)	0.110(11)	0.248(3)
C(31)	−0.1999(6)	0.0060(6)	0.2340(3)	0.050(4)	0.752(3)	C(71)	−0.109(2)	−0.236(2)	0.2684(11)	0.064(7)	0.248(3)
C(32)	−0.2356(6)	0.0395(6)	0.2045(3)	0.049(4)	0.752(3)	C(72)	−0.103(2)	−0.2352(19)	0.2167(11)	0.064(7)	0.248(3)
H(32)	−0.2466(10)	0.0240(9)	0.1655(5)	0.081(11)	0.752(3)	H(72)	−0.113(3)	−0.193(3)	0.1949(15)	0.110(11)	0.248(3)
C(33)	−0.2570(7)	0.0929(6)	0.2252(4)	0.068(6)	0.752(3)	C(73)	−0.085(2)	−0.289(2)	0.1929(9)	0.064(7)	0.248(3)
H(33)	−0.2847(11)	0.1190(10)	0.2022(6)	0.122(17)	0.752(3)	H(73)	−0.081(4)	−0.289(3)	0.1527(10)	0.110(11)	0.248(3)
C(34)	−0.2427(8)	0.1129(6)	0.2756(4)	0.074(6)	0.752(3)	C(74)	−0.073(3)	−0.343(2)	0.2209(13)	0.064(7)	0.248(3)
H(34)	−0.2593(12)	0.1545(10)	0.2918(6)	0.129(19)	0.752(3)	H(74)	−0.059(4)	−0.385(3)	0.2024(17)	0.110(11)	0.248(3)
C(35)	−0.2070(8)	0.0794(7)	0.3051(3)	0.096(8)	0.752(3)	C(75)	−0.078(3)	−0.344(2)	0.2726(12)	0.064(7)	0.248(3)
H(35)	−0.1959(12)	0.0949(11)	0.3441(5)	0.20(4)	0.752(3)	H(75)	−0.069(4)	−0.386(3)	0.2944(17)	0.110(11)	0.248(3)
C(36)	−0.1856(7)	0.0260(7)	0.2843(3)	0.074(6)	0.752(3)	C(76)	−0.096(3)	−0.290(2)	0.2964(9)	0.064(7)	0.248(3)
H(36)	−0.1580(11)	0.0001(11)	0.3072(5)	0.15(2)	0.752(3)	H(76)	−0.101(4)	−0.290(3)	0.3366(10)	0.110(11)	0.248(3)
C(41)	−0.1696(5)	−0.0483(5)	0.1556(2)	0.035(3)	0.752(3)	C(81)	−0.1326(18)	−0.177(2)	0.3490(10)	0.052(6)	0.248(3)
C(42)	−0.2285(4)	−0.1059(4)	0.1245(3)	0.040(4)	0.752(3)	C(82)	−0.0605(16)	−0.127(2)	0.3736(12)	0.052(6)	0.248(3)
H(42)	−0.2801(8)	−0.1583(8)	0.1403(4)	0.085(12)	0.752(3)	H(82)	−0.0080(19)	−0.084(3)	0.3527(17)	0.110(11)	0.248(3)
C(43)	−0.2211(5)	−0.0960(5)	0.0729(2)	0.044(4)	0.752(3)	C(83)	−0.056(2)	−0.131(2)	0.4252(13)	0.052(6)	0.248(3)
H(43)	−0.2668(8)	−0.1406(8)	0.0488(4)	0.087(11)	0.752(3)	H(83)	0.000(3)	−0.092(3)	0.4443(18)	0.110(11)	0.248(3)
C(44)	−0.1547(5)	−0.0285(5)	0.0525(2)	0.043(4)	0.752(3)	C(84)	−0.123(3)	−0.186(3)	0.4521(10)	0.052(6)	0.248(3)
H(44)	−0.1490(8)	−0.0207(7)	0.0123(4)	0.085(12)	0.752(3)	H(84)	−0.120(4)	−0.190(4)	0.4922(10)	0.110(11)	0.248(3)
C(45)	−0.0958(5)	0.0291(5)	0.0836(3)	0.066(6)	0.752(3)	C(85)	−0.196(2)	−0.236(2)	0.4275(14)	0.052(6)	0.248(3)
H(45)	−0.0444(8)	0.0813(8)	0.0679(4)	0.104(14)	0.752(3)	H(85)	−0.248(3)	−0.279(3)	0.4484(19)	0.110(11)	0.248(3)
C(46)	−0.1032(5)	0.0192(5)	0.1352(3)	0.066(5)	0.752(3)	C(86)	−0.2002(17)	−0.232(2)	0.3759(14)	0.052(6)	0.248(3)
H(46)	−0.0573(8)	0.0640(8)	0.1594(4)	0.111(18)	0.752(3)	H(86)	−0.256(2)	−0.271(3)	0.3568(19)	0.110(11)	0.248(3)
H(1B)	−0.010(17)	−0.050(6)	0.205(2)	0.072(14)	0.0826(10)						

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. ^b The atoms from H(1A) to H(46) correspond to the major tetramer, whereas the atoms from H(1B) to H(86) correspond to the minor tetramer.

widths (fwhm) of 15.8 Hz. With decreasing temperature, the line width of each peak increases and only a single peak is discernible below about 248 K. Below this temperature, we cannot assess whether there is strictly a single peak or two (or more) peaks unresolved from each other (with the peak separation substantially less than the line width). The increase of line width on decreasing temperature is presumably due to the effects of the motion of the hydroxyl hydrogens (rotation about the ^{13}C —OH bonds) on the relaxation properties of the ^{13}C nuclei.

In summary, the two peaks observed (in 3:1 intensity ratio) at ambient temperature presumably reflect different local environments in the tetramer. We discuss the assignment of these local environments in section 4.

4. Discussion

In the average crystal structure determined from diffraction studies, one molecule in each tetramer (the “apical” molecule)

is crystallographically independent of the other three molecules (the “basal” molecules), which are related to each other by the space group symmetry. The overall molecular packing of tetramers in the crystal structure gives rise to space group $R\bar{3}$, which dictates that the point symmetry of the tetramer is C_3 . However, the symmetry of each tetramer (in the average crystal structure) is actually approximated well by the higher symmetry point group T . Thus, in the O_4 core of the tetramer, all $\text{O}\cdots\text{O}$ distances are equal within the precision of the experimental determination, and in the average crystal structure, each hydroxyl group in the tetramer has essentially the same local environment. We recall that the crystal structure determined from diffraction data is a space-averaged (averaged over all unit cells) and time-averaged representation of the true crystal structure. Thus, the fact that all four hydroxyl groups in the tetramer in the average crystal structure have essentially identical environments does not necessarily imply that all four hydroxyl groups are equivalent at a sufficiently local level (e.g., for a given tetramer observed

TABLE 4: Final Refined Fractional Coordinates, Equivalent Isotropic Displacement Parameters (U_{eq}) and Occupancies for the Crystal Structure of Triphenylmethanol Determined at 293 and 113 K from Single-Crystal X-ray Diffraction Data

	x	y	z	$U_{eq}/\text{\AA}^2$	occupancy		x	y	z	$U_{eq}/\text{\AA}^2$	occupancy
293 K											
O(1)	0	0	0.32048(13)	0.0912(14)	0.776(2)	O(3)	0	0	0.1889(4)	0.086(4)	0.224(2)
C(1)	0	0	0.3744(2)	0.0622(14)	0.776(2)	C(3)	0	0	0.1347(6)	0.059(4)	0.224(2)
O(2)	-0.09796(14)	-0.0310(2)	0.23216(10)	0.0961(10)	0.776(2)	O(4)	-0.0741(5)	-0.0975(5)	0.2761(4)	0.090(3)	0.224(2)
C(2)	-0.1763(2)	-0.0532(2)	0.21301(12)	0.0657(9)	0.776(2)	C(4)	-0.1320(6)	-0.1786(6)	0.2925(4)	0.062(3)	0.224(2)
C(11)	-0.0602(2)	-0.0842(2)	0.39182(11)	0.0632(8)	0.776(2)	C(51)	-0.0831(5)	-0.0220(6)	0.1170(4)	0.066(3)	0.224(2)
C(12)	-0.1308(2)	-0.1296(2)	0.3661(2)	0.0862(12)	0.776(2)	C(52)	-0.1482(6)	-0.0760(7)	0.1452(4)	0.081(4)	0.224(2)
C(13)	-0.1882(3)	-0.2035(3)	0.3827(2)	0.100(2)	0.776(2)	C(53)	-0.2254(5)	-0.0982(9)	0.1302(6)	0.151(18)	0.224(2)
C(14)	-0.1744(5)	-0.2311(4)	0.4263(3)	0.115(3)	0.776(2)	C(54)	-0.2375(7)	-0.0663(11)	0.0869(6)	0.131(9)	0.224(2)
C(15)	-0.1045(5)	-0.1894(4)	0.4513(2)	0.104(2)	0.776(2)	C(55)	-0.1725(10)	-0.0122(11)	0.0587(5)	0.128(12)	0.224(2)
C(16)	-0.0491(3)	-0.1171(5)	0.4345(2)	0.080(2)	0.776(2)	C(56)	-0.0953(8)	0.0099(9)	0.0737(4)	0.110(12)	0.224(2)
C(21)	-0.2341(2)	-0.1374(2)	0.23056(13)	0.0702(9)	0.776(2)	C(61)	-0.2136(5)	-0.1957(6)	0.2746(4)	0.059(3)	0.224(2)
C(22)	-0.2103(3)	-0.1938(3)	0.2343(2)	0.0932(13)	0.776(2)	C(62)	-0.2314(6)	-0.1345(5)	0.2785(4)	0.099(5)	0.224(2)
C(23)	-0.2641(5)	-0.2708(3)	0.2479(4)	0.112(4)	0.776(2)	C(63)	-0.3059(8)	-0.1474(8)	0.2637(5)	0.101(8)	0.224(2)
C(24)	-0.3409(5)	-0.2962(4)	0.2569(3)	0.141(3)	0.776(2)	C(64)	-0.3626(6)	-0.2215(10)	0.2451(6)	0.089(7)	0.224(2)
C(25)	-0.3656(4)	-0.2427(5)	0.2541(3)	0.145(3)	0.776(2)	C(65)	-0.3449(8)	-0.2828(7)	0.2413(7)	0.093(7)	0.224(2)
C(26)	-0.3134(3)	-0.1634(3)	0.2403(3)	0.105(2)	0.776(2)	C(66)	-0.2703(8)	-0.2698(6)	0.2560(6)	0.118(17)	0.224(2)
C(31)	-0.1988(2)	0.0066(2)	0.23335(13)	0.0702(9)	0.776(2)	C(71)	-0.1080(6)	-0.2358(6)	0.2694(3)	0.060(3)	0.224(2)
C(32)	-0.2352(3)	0.0380(3)	0.2058(2)	0.0915(13)	0.776(2)	C(72)	-0.0950(7)	-0.2321(6)	0.2183(3)	0.099(5)	0.224(2)
C(33)	-0.2561(5)	0.0919(6)	0.2249(3)	0.119(2)	0.776(2)	C(73)	-0.0753(9)	-0.2847(9)	0.1958(4)	0.101(7)	0.224(2)
C(34)	-0.2422(5)	0.1123(6)	0.2729(3)	0.123(2)	0.776(2)	C(74)	-0.0686(10)	-0.3411(9)	0.2243(6)	0.078(7)	0.224(2)
C(35)	-0.2059(6)	0.0814(7)	0.3015(2)	0.135(3)	0.776(2)	C(75)	-0.0816(11)	-0.3449(9)	0.2753(6)	0.102(10)	0.224(2)
C(36)	-0.1844(3)	0.0293(3)	0.2825(2)	0.110(2)	0.776(2)	C(76)	-0.1013(10)	-0.2923(9)	0.2979(4)	0.099(9)	0.224(2)
C(41)	-0.1698(2)	-0.0483(2)	0.15611(12)	0.0638(8)	0.776(2)	C(81)	-0.1295(5)	-0.1810(5)	0.3492(3)	0.056(2)	0.224(2)
C(42)	-0.2274(2)	-0.1036(3)	0.1253(2)	0.076(2)	0.776(2)	C(82)	-0.0595(5)	-0.1307(6)	0.3749(4)	0.077(3)	0.224(2)
C(43)	-0.2219(3)	-0.0941(3)	0.0742(2)	0.0955(14)	0.776(2)	C(83)	-0.0572(7)	-0.1354(9)	0.4264(4)	0.092(11)	0.224(2)
C(44)	-0.1580(3)	-0.0308(4)	0.0530(2)	0.0920(14)	0.776(2)	C(84)	-0.1248(9)	-0.1904(12)	0.4523(3)	0.072(7)	0.224(2)
C(45)	-0.0990(3)	0.0244(4)	0.0836(2)	0.100(2)	0.776(2)	C(85)	-0.1948(7)	-0.2407(9)	0.4267(4)	0.062(5)	0.224(2)
C(46)	-0.1048(2)	0.0153(3)	0.1339(2)	0.0942(13)	0.776(2)	C(86)	-0.1972(5)	-0.2360(6)	0.3751(4)	0.090(6)	0.224(2)
113 K											
O(1)	0	0	0.3200(2)	0.083(2)	0.769(2)	O(3)	0	0	0.1910(5)	0.074(5)	0.231(2)
C(1)	0	0	0.3740(2)	0.0504(15)	0.769(2)	C(3)	0	0	0.1367(6)	0.046(4)	0.231(2)
O(2)	-0.0974(2)	-0.0310(3)	0.23286(13)	0.0932(12)	0.769(2)	O(4)	-0.0788(5)	-0.0956(6)	0.2768(4)	0.076(3)	0.231(2)
C(2)	-0.1764(2)	-0.0536(3)	0.21319(14)	0.0574(10)	0.769(2)	C(4)	-0.1350(7)	-0.1789(7)	0.2927(5)	0.053(3)	0.231(2)
C(11)	-0.0612(2)	-0.0852(2)	0.39172(13)	0.0502(9)	0.769(2)	C(51)	-0.0843(6)	-0.0229(7)	0.1179(4)	0.060(3)	0.231(2)
C(12)	-0.1319(3)	-0.1316(3)	0.3648(2)	0.0720(12)	0.769(2)	C(52)	-0.1481(7)	-0.0733(7)	0.1490(4)	0.079(5)	0.231(2)
C(13)	-0.1909(3)	-0.2062(3)	0.3816(2)	0.080(2)	0.769(2)	C(53)	-0.2267(6)	-0.0939(9)	0.1365(5)	0.074(9)	0.231(2)
C(14)	-0.1789(5)	-0.2350(5)	0.4251(3)	0.094(3)	0.769(2)	C(54)	-0.2415(7)	-0.0641(10)	0.0928(6)	0.138(9)	0.231(2)
C(15)	-0.1089(6)	-0.1919(4)	0.4526(2)	0.078(2)	0.769(2)	C(55)	-0.1778(9)	-0.0137(10)	0.0618(5)	0.090(7)	0.231(2)
C(16)	-0.0510(3)	-0.1179(5)	0.4356(3)	0.059(2)	0.769(2)	C(56)	-0.0992(8)	0.0069(8)	0.0743(4)	0.088(10)	0.231(2)
C(21)	-0.2351(2)	-0.1394(3)	0.23025(14)	0.0606(10)	0.769(2)	C(61)	-0.2193(6)	-0.1959(6)	0.2749(4)	0.051(3)	0.231(2)
C(22)	-0.2111(3)	-0.1973(3)	0.2348(2)	0.0797(14)	0.769(2)	C(62)	-0.2383(6)	-0.1351(5)	0.2811(4)	0.084(5)	0.231(2)
C(23)	-0.2657(6)	-0.2757(4)	0.2480(3)	0.099(3)	0.769(2)	C(63)	-0.3144(8)	-0.1487(8)	0.2678(6)	0.088(6)	0.231(2)
C(24)	-0.3437(5)	-0.3011(4)	0.2557(3)	0.111(2)	0.769(2)	C(64)	-0.3715(6)	-0.2231(9)	0.2483(6)	0.078(8)	0.231(2)
C(25)	-0.3694(4)	-0.2458(5)	0.2513(3)	0.100(2)	0.769(2)	C(65)	-0.3525(7)	-0.2839(7)	0.2422(6)	0.063(5)	0.231(2)
C(26)	-0.3165(3)	-0.1655(3)	0.2396(2)	0.0773(13)	0.769(2)	C(66)	-0.2763(8)	-0.2703(6)	0.2555(5)	0.085(11)	0.231(2)
C(31)	-0.2000(2)	0.0066(3)	0.23387(15)	0.0593(10)	0.769(2)	C(71)	-0.1106(7)	-0.2364(6)	0.2691(4)	0.052(3)	0.231(2)
C(32)	-0.2351(3)	0.0392(3)	0.2056(2)	0.0676(12)	0.769(2)	C(72)	-0.1002(7)	-0.2338(6)	0.2177(4)	0.089(5)	0.231(2)
C(33)	-0.2571(5)	0.0938(6)	0.2254(3)	0.089(2)	0.769(2)	C(73)	-0.0803(9)	-0.2868(8)	0.1947(4)	0.083(6)	0.231(2)
C(34)	-0.2432(5)	0.1141(5)	0.2745(3)	0.097(2)	0.769(2)	C(74)	-0.0709(9)	-0.3423(8)	0.2231(5)	0.064(7)	0.231(2)
C(35)	-0.2085(6)	0.0801(7)	0.3033(3)	0.110(3)	0.769(2)	C(75)	-0.0813(10)	-0.3449(9)	0.2746(5)	0.078(7)	0.231(2)
C(36)	-0.1869(4)	0.0274(4)	0.2838(2)	0.094(2)	0.769(2)	C(76)	-0.1011(9)	-0.2919(9)	0.2976(3)	0.079(9)	0.231(2)
C(41)	-0.1692(2)	-0.0483(3)	0.15599(15)	0.0555(10)	0.769(2)	C(81)	-0.1323(5)	-0.1813(6)	0.3499(3)	0.049(3)	0.231(2)
C(42)	-0.2278(3)	-0.1061(4)	0.1237(2)	0.0596(14)	0.769(2)	C(82)	-0.0613(5)	-0.1291(6)	0.3750(4)	0.054(3)	0.231(2)
C(43)	-0.2203(3)	-0.0936(3)	0.0731(2)	0.0646(11)	0.769(2)	C(83)	-0.0576(7)	-0.1328(9)	0.4266(4)	0.060(9)	0.231(2)
C(44)	-0.1551(3)	-0.0288(3)	0.0518(2)	0.0674(12)	0.769(2)	C(84)	-0.1250(10)	-0.1886(12)	0.4533(3)	0.055(7)	0.231(2)
C(45)	-0.0972(3)	0.0278(4)	0.0840(2)	0.081(2)	0.769(2)	C(85)	-0.1960(8)	-0.2408(10)	0.4282(4)	0.045(5)	0.231(2)
C(46)	-0.1035(3)	0.0172(3)	0.1345(2)	0.083(2)	0.769(2)	C(86)	-0.1996(5)	-0.2372(7)	0.3766(4)	0.067(6)	0.231(2)

^a The atoms from O(1) to C(46) correspond to the major tetramer, whereas the atoms from O(3) to C(86) correspond to the minor tetramer.

TABLE 5: O...O Distances for the Major Tetramer of Triphenylmethanol Determined from the Neutron and X-ray Diffraction Data

	$O_{apical} \cdots O_{basal}/\text{\AA}$	$O_{basal} \cdots O_{basal}/\text{\AA}$
100 K (neutron)	2.90(2)	2.90(2)
293 K (X-ray)	2.905(4)	2.901(4)
113 K (X-ray)	2.859(5)	2.854(5)

over a specific period of time). Indeed, our ^{13}C NMR results suggest that, at a sufficiently local level, all four hydroxyl groups in the tetramer are *not* equivalent. Thus, the average picture in which all four hydroxyl groups have essentially equivalent environments *may* be the result of static and/or dynamic disorder between different local and/or instantaneous structural situations.

There is an *apparent* dilemma in bringing together informa-

tion on the spatial distribution of the hydroxyl hydrogens conveyed by the average crystal structure and information on the spatial distribution of the hydroxyl hydrogens implicated by the dynamic model determined from ^2H NMR spectroscopy. Our ^2H NMR results³ on PhCOD show clearly that each hydroxyl group is dynamic (by rotation about the C—OD bond) on the time scale (10^{-3} – 10^{-8} s) of the ^2H NMR technique used. Other slower motions (time scale greater than 10^{-3} s) may also occur, although they will not be evident from these ^2H NMR experiments. The dynamic model derived from the ^2H NMR results has two dynamically distinguishable types of deuterons, interpreted as a unique hydroxyl group (type d¹) in the tetramer undergoing three-site 120° jumps and the other three hydroxyl groups (type d³) in the tetramer undergoing two-site 120° jumps.

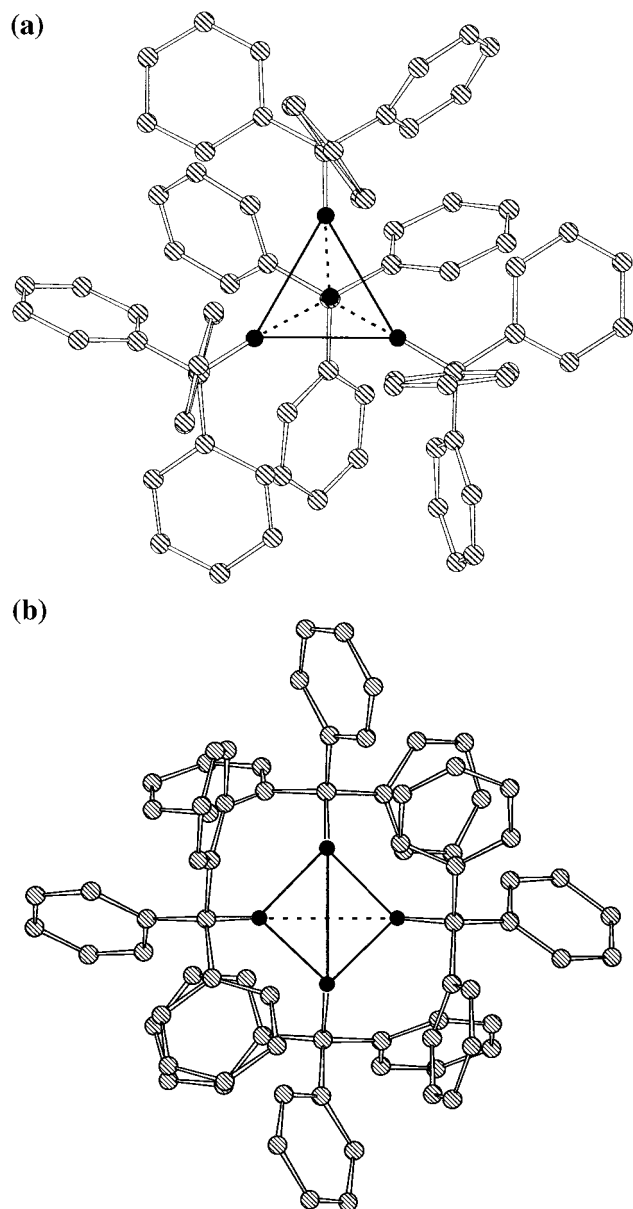


Figure 5. Tetramer in the average crystal structure of triphenylmethanol determined at 100 K from neutron diffraction data, viewed (a) along the C—O bond of one of the basal molecules (a 3-fold axis in the approximate T symmetry of the tetramer) and (b) along one of the 2-fold axes in the approximate T symmetry of the tetramer.

Assuming that the sites occupied by the hydroxyl deuterons correspond to O—D \cdots O hydrogen bonds, the hydroxyl hydrogen for each d^3 molecule samples sites on only two of the three available O \cdots O edges of the tetramer (within the ^2H NMR time scale). Although it may be tempting to assign the unique d^1 site in the dynamic model to the unique “apical” molecule in the tetramer in the average crystal structure, and thus to assign the three d^3 sites in the dynamic model to the three “basal” molecules in the tetramer in the average crystal structure, there is no a priori reason to make such an assignment, and indeed such an assignment would lead to the following dilemma. If all d^3 sites did correspond to “basal” molecules, the hydroxyl hydrogen of each “basal” molecule in the average crystal structure should be disordered only between two sites rather than among the three sites observed in the average crystal structure. To reconcile this situation, we propose that, on averaging over all tetramers in the crystal [static disorder] and/or on averaging over the time scale of the neutron diffraction

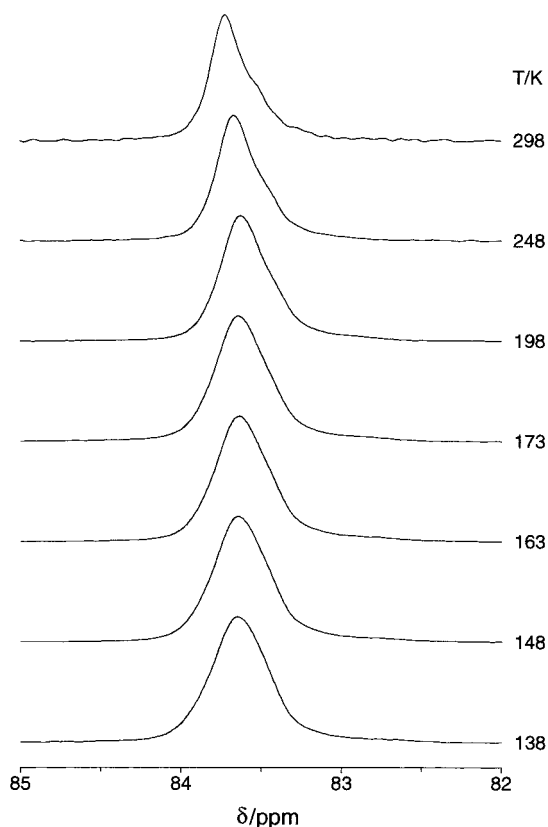


Figure 6. High-resolution solid-state ^{13}C NMR spectra recorded for $\text{Ph}_3^{13}\text{COH}$ in the temperature range 298–138 K. Only the region of the spectrum corresponding to the labeled ^{13}C environment is shown.

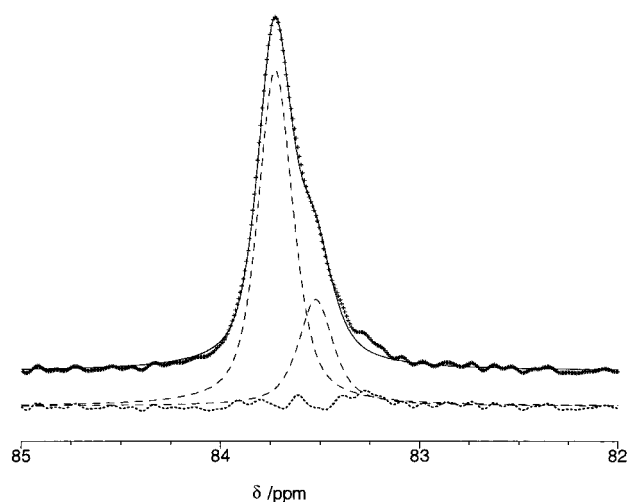


Figure 7. Fitting of the resonance due to the $\text{Ph}_3^{13}\text{COH}$ environment in the high-resolution solid-state ^{13}C NMR spectrum recorded at 298 K. The experimental line shape (+), the overall fitted line shape (solid line), the two peaks contributing to the fitted line shape (dashed lines), and the difference between the experimental and fitted line shapes (dotted line (bottom)) are shown. The fitted line shape is based on two peaks with an intensity ratio of 3:1. The peaks are of mixed Gaussian/Lorentzian character (40% Gaussian for the higher intensity peak; 30% Gaussian for the lower intensity peak), the line width for each peak is 15.8 Hz, and the peak separation is 0.20 ppm (15.1 Hz).

measurement (several hours) [dynamic disorder], the unique d^1 site must be distributed with essentially equal probability over all four molecules in the tetramer. The two peaks observed (in 1:3 intensity ratio) in our ^{13}C NMR spectrum may be assigned as different local environments for the d^1 and d^3 sites in the tetramer.

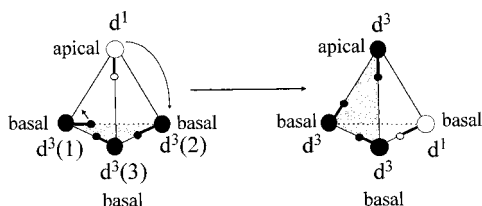


Figure 8. Proposed mechanism for dynamic disorder involving migration of the d^1 site (empty circles) from one molecule, with a corresponding migration of the face defined by the three d^3 sites (filled circles). Reorientation of the hydroxyl groups about the C—OH bonds are effective on the ^2H NMR time scale and are substantially faster than the migration of the d^1 site. Note that the assignment of the molecules as apical or basal refers to the average crystal structure, whereas classification as d^1 or d^3 refers to the dynamic model determined from ^2H NMR spectroscopy.

In the case of static disorder, the d^1 site in a given tetramer would always be associated with the same molecule, which may (with equal probability) be the apical molecule or any of the basal molecules. In this case, it may be expected that the carbon atom of the d^1 site should experience a different local environment from the carbon atoms of the d^3 sites, but averaging these local structural situations over the whole crystal would result in the essentially tetrahedral local geometry of the tetramer observed in the average crystal structure.

In the case of dynamic disorder, for each tetramer in the crystal, the d^1 site would be required to migrate from one molecule to another within the tetramer such that the probability that the d^1 site resides on the apical molecule is equal to the probability that it resides on any of the three basal molecules. At any instant in time, it may be expected that the d^1 site should experience a different local environment from the d^3 site, but averaging these local situations over the time scale of the motion [which is presumably short with respect to the time scale of the neutron diffraction measurement (several hours)] would result in the essentially tetrahedral geometry of the tetramer observed in the average crystal structure. Since the dynamic model derived from our ^2H NMR results does not invoke any exchange between deuterons of types d^1 and d^3 , it is clear that the time scale for migration of the unique d^1 site among the four molecules in the tetramer must be longer than the characteristic time scale of the ^2H NMR technique ($\tau > 10^{-3}$ s) and furthermore must be longer than the time scale corresponding to our ^{13}C NMR measurements ($\tau > 0.07$ s) [i.e., the rate of this motion must be slower than the frequency separation (15.1 Hz at 298 K) between the two peaks observed in the ^{13}C NMR spectrum]. Such ultraslow motion may be appropriate for investigation by two-dimensional ^2H NMR exchange experiments.

If the disorder of the d^1 site is dynamic, a straightforward mechanism for migration of the d^1 site among the four molecules in the tetramer can be proposed (see Figure 8). In this mechanism, one d^3 hydroxyl group (denoted by subscript $d^3(1)$) in the tetramer switches from hydrogen bonding along the $\text{O}_{d^3(1)}\cdots\text{O}_{d^3(2)}$ edge of the tetramer to the $\text{O}_{d^3(1)}\cdots\text{O}_{d^1}$ edge (where subscript d^1 denotes the d^1 site before the switch). The previous d^1 site becomes a new d^3 site, and the previous d^3 site denoted by subscript $d^3(2)$ becomes the new d^1 site. Presumably the activation energy for this hydrogen bond switch is significantly higher than the activation energies³ for the three-site 120° jump motion of the hydroxyl group of the d^1 molecule (ca. 10 kJ mol^{-1}) and the two-site 120° jump motion of the hydroxyl groups of the d^3 molecules (ca. 21 kJ mol^{-1}). This suggestion

is particularly reasonable, since the *local* structure of the tetramer is expected to be distorted from the *average* (approximately tetrahedral) structure of the tetramer in the average crystal structure, as implied by our ^{13}C NMR results. For example, if the $\text{O}_{d^3}\cdots\text{O}_{d^3}$ distances and $\text{O}_{d^3}\cdots\text{O}_{d^1}$ distances could be determined directly on a time scale shorter than the lifetime of the d^1 and d^3 sites (but longer than the time scale for the rotational motions of the hydroxyl groups established from ^2H NMR), the $\text{O}_{d^3}\cdots\text{O}_{d^3}$ distances would be expected to be shorter than the $\text{O}_{d^3}\cdots\text{O}_{d^1}$ distances, since the $\text{O}_{d^3}\cdots\text{O}_{d^3}$ edges have an average of one O—H \cdots O hydrogen bond whereas the $\text{O}_{d^3}\cdots\text{O}_{d^1}$ edges have an average of one-third of an O—H \cdots O hydrogen bond.

In summary, at a sufficiently local level (with respect to space and/or time) one site in each tetramer must be unique (i.e., the d^1 site of the dynamic model determined from ^2H NMR), which may be expected to give rise locally and/or instantaneously to different $\text{O}_{d^3}\cdots\text{O}_{d^1}$ and $\text{O}_{d^3}\cdots\text{O}_{d^3}$ distances in the tetramer. However, the disorder among these different local structures leads to all molecules in the tetramer being essentially equivalent in the average crystal structure, as reflected by the approximate tetrahedral symmetry. At present, we cannot deduce whether this disorder is static or dynamic, although from our ^{13}C NMR results it is clear that if the disorder is dynamic, the migration of the d^1 site must occur on a time scale longer than ca. 0.07 s. The nominal C_3 symmetry of the tetramer deduced from the space group of the average crystal structure is a consequence of the overall packing of different tetramers with respect to each other, and the actual (approximate) symmetry of the tetramer in the average crystal structure is higher. In general, we recall that high symmetry building units may be arranged in a lower symmetry crystal structure (consider, for example, the crystal structure of benzene¹⁰), although the high symmetry building unit may nevertheless be distorted through its interaction with the lower symmetry environment. Thus, the actual symmetry of the building unit may be lowered to reflect the symmetry of its environment but may still be approximated well by the higher symmetry.

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