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Five-Membered Ring Rotations, Pseudorotations, and Hydrogen Bond Exchange Dynamics in the Solid State Studied by NMR Spectroscopy

Frank G. Riddell,[*,†] **Kenneth S. Cameron,**[†] **Susan A. Holmes,**[‡] and **John H. Strange**[‡]

Contribution from The School of Chemistry, The University of St. Andrews, St. Andrews KY16 9ST, Scotland, UK, and The Physics Laboratory, The University of Kent, Canterbury, CT2 7NR, Kent, UK

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Abstract: ^{13}C CP/MAS NMR studies were carried out on *trans*-1,2-cyclopentanediol, on 4,4-dimethyl-*trans*-1,2-cyclopentanediol, and on sulfolane at variable temperatures. The spectra showed evidence of three dynamic solid-state processes: hydrogen bond exchange, ring pseudorotation, and whole molecule rotations about local C_2 axes. Fitting of $T_{1\rho}$ data to calculated values of the [13]C−[1]H dipolar interactions allowed differentiation between ring pseudorotations and whole molecule C_2 reorientations. Isotopic ^{1}H/^{2}H substitution demonstrated the existence of hydrogen bond exchange processes in the diols. Activation parameters for these processes were derived from both coalescence measurements and the $T_{1\rho}$ measurements.

Introduction

NMR spectroscopy is ideally suited for measurements of molecular dynamics, particularly in solids, where a wide range of methods is available for such investigations.[1] We and others[2−14] have shown that CP/MAS NMR methods can be used to study intramolecular motions. Our guiding principle in searching for such motions has been that those motions that cause the least distress to the crystal environment around a molecule should be the most readily observed by NMR methods. The principle of least distress[2] has proved fruitful in suggesting groups that should show observable conformational motions in solids. In particular many of our experiments have been performed on compounds containing groups of high local symmetry such as *tert*-butyl derivatives.

Another type of conformational motion that should cause little distress to the crystal environment is the pseudorotation of five-membered rings. Pseudorotation of cyclopentane was first discussed by Kilpatrick *et al.* in 1947.[15] They showed that the puckering of the cyclopentane ring is not of a definite type, that two coordinates are needed to specify the process, a puckering amplitude and the phase of the maximum puckering, and that the phase of maximum puckering travels essentially freely around the ring. A suitable definition for a pseudorotation in cyclic molecules such as cyclopentane, twist cyclohexane, and cycloheptane is that given by Hendrickson,[16] as the passage of a ring with a plane of symmetry through an atom to one with an axis of symmetry bisecting the bond adjacent to the atom and *vice versa*. In an isolated cyclopentane molecule pseudorotation is essentially free. In the solid the additional constraints imposed by neighboring molecules would be expected to raise the barrier to the pseudorotation process and possibly reduce the maximum amplitude for the process. A review of the conformational analysis of cyclopentane and other cyclic and acyclic hydrocarbons can be found in ref 17.

Planar cyclopentane has severe eclipsing strain along its five C−C bonds which can be overcome in two ways that maintain some of the original symmetry of the molecule. Maintaining the C_s plane through one methylene group by moving it above or below the plane of the other four carbons gives rise to a so-called envelope conformation. Maintaining the C_2 axis through the center of a C−C bond and the CH$_2$ opposite to it on the ring whilst moving the adjacent carbons above and below the plane of the remaining three gives rise to a so called twist conformation. Therefore, according to Hendrickson's definition[16] the passage of a twist (C_2 symmetry) into an envelope (C_s symmetry) and onto the next twist is a pseudorotation process.

Calculations[18] based on gas phase mid infrared measurements[19,20] show that in the course of this pseudorotation of the

* Proofs to: Dr. F. G. Riddell, School of Chemistry, The University of St. Andrews, St. Andrews, KY16 9ST, Scotland.
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isolated cyclopentane molecule, the envelope has a flap angle of 35° and the twist a dihedral angle of 21°.

An early ^{1}H NMR study of solid cyclopentane by second moment and T_1 measurements shows very little molecular motion in the solid below 120 K, but the phase transition at 122 K introduces significant molecular motion in the solid.[21] Molecular motions in derivatives of cyclopentane should, of course, be different as they will be affected both by the inclusion of the substituents and by the altered intermolecular interactions.

A recent ^{2}H study of the conformational dynamics in solid cyclopentane[22] puts forward the idea that pseudorotation in cyclopentane is accompanied by a "wobbling" motion about the C_5 axis. The apparent pucker angle was interpreted as a true inherent puckering angle of 25 degrees plus a small additional wobble of 5−10 degrees. We see no evidence of this in the samples discussed here which is unsurprising given the lower symmetry of our molecules.

Two interesting CP/MAS NMR studies of five-membered rings were reported recently by Lambert *et al.*[12,13] Although the interpretation of their results was hindered by the paucity of X-ray crystallographic structural data and multiple phase changes, they were nonetheless able to demonstrate the existence of separate conformations and of conformational motions in the compounds they studied. One complication in Lambert's work was due to the fact that several of the compounds they studied were alcohols, and so hydrogen bonding was potentially involved in some of the dynamic phenomena they observed.

Several CP/MAS NMR methods for the study of dynamic processes in solids are available.[1] The general rule is that when the frequency of the molecular motion is similar to that of an NMR interaction, effects are observable in the spectrum. Rates measurable by dynamic line shape changes are comparable to the chemical shift difference and typically fall into the range 10^2-10^4 s^{-1}. Rates measurable by $T_{1\rho}$ measurements can be made when the rate of the molecular motion is similar to the precessional frequency of the nuclei in the spin locking field, typically 50−100 kHz.[3,23] Such rates typically extend from ca. 10^4 to as high as 10^7 s^{-1}. Similar, but not identical is the method of so called maximum dipolar broadening.[24] This occurs when the frequency of the molecular motion, which lacks a phase coherence, is similar to and so interferes with the phase coherent precessional frequency of ^{1}H in the dipolar decoupling field. This gives a single rate at the precessional frequency of the ^{1}H nuclei in the decoupling field. It should be noted that, when performing $T_{1\rho}$ measurements, if the ^{13}C spin lock field and the decoupler power are the same as during the Hartman−Hahn condition, maximum dipolar broadening will occur at the same temperature as the $T_{1\rho}$ minimum. Importantly, the derivation of rates of molecular motions from relaxation time measurements is independent of whether there is a coalescence phenomenon possible or not. Thus, $T_{1\rho}$ measurements will provide activation data for rotations of both the phenyl and *tert*-butyl groups[2−5,8,10,11] that display coalescence phenomena of the site exchange type and for the isopropyl and *tert*-amyl groups that do not[8] because they have a single preferred conformation. The range of rates can equally be extended in the lower limit by magnetization transfer or 2D CPEXSY measurements where rates comparable with ^{13}C spin−lattice relaxation times are accessible.[25,26] Using such methods we have measured rates

as low as 10 s^{-1}. Thus six orders of magnitude in rates of rotation are, in principle, available for study using these ^{13}C CP/MAS NMR techniques with almost continuous coverage of the range. The range may, in suitable cases, be extended further by use of T_1 and T_2 measurements.[1]

Some further points need to be made with regard to changes in $T_{1\rho}$ and with respect to $T_{1\rho}$ minima (see ref 3 for a more detailed theory) since these are used in the current work. Cross polarized spectra require a transfer of polarization from ^{1}H to ^{13}C which occurs at a given rate with time constants in the millisecond range. Whilst the polarization is being transferred, it is also being lost from both the ^{1}H and ^{13}C reservoirs by the $T_{1\rho}$ mechanism. Thus, efficient $T_{1\rho}$ relaxation leads to a reduction in signal intensity in CP spectra. If relaxation is dominated by modulation of nuclear dipole−dipole interactions reorientation rates may be calculated from $T_{1\rho}$ data by observation of the minimum and knowledge of the precessional frequency of the ^{13}C nuclei in the spin locking field (ω_1). $T_{1\rho}$ minima will be deeper for groups with larger modulation of their dipolar interactions. For example, a methyl rotation can cause extremely efficient $T_{1\rho}$ relaxation for the central carbon, whereas the central carbon in a *tert*-butyl group with no directly bound ^{1}H is less efficiently relaxed by this mechanism. The dipolar interaction that governs the $T_{1\rho}$ relaxation can be explicitly calculated from a known or assumed molecular geometry and a jump model for a proposed molecular motion. Such calculations can, in principle, differentiate between various possible modes of molecular motion, and we show in this paper an example of this.

Lambert *et al.*[12,13] reported several examples of maximum dipolar broadening in the compounds they studied but did not attempt to measure the associated changes in $T_{1\rho}$ that could give information on the dynamics of the processes involved. In particular they demonstrated that *trans*-1,2-cyclopentanediol and sulfolane show striking maximum dipolar broadening. Therefore, measurement of the associated $T_{1\rho}$ values should enable (at least) the derivation of the associated energies of activation and potentially assignment of the mode of motion. Accordingly, we set out to measure these parameters and also we examined the closely related compound 4,4-dimethyl-*trans*-1,2-cyclopentanediol.

The participation of hydrogen bond making and breaking should be capable of investigation by preparing the O−[2]H derivatives of the diols and comparing the activation parameters obtained from the NMR spectra of both isotopically substituted derivatives. Small differences in rates are particularly well distinguished at or around coalescence temperatures. We thus hoped to clarify the work of Lambert et al. and to attempt to prove the contribution or otherwise of hydrogen bond making and breaking to the observed solid-state processes.

Experimental Section

NMR Spectra. Solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker MSL 500 spectrometer at 125.758 MHz using 4 mm o.d. zirconia rotors. The following typical conditions were employed: contact time 1 ms, spectral width 30,000 Hz, acquisition time 17.4 ms, spin locking field frequency ca. 50 kHz, recycle delay 5 s, spinning speeds 4−8 kHz. Chemical shifts were referenced to the CH_2 resonance in an external adamantane sample at 38.56 ppm. Dipolar dephased (Non Quaternary Suppressed (NQS)) spectra to aid spectral assignments were obtained by a standard sequence incorporating a 50 μs dipolar dephasing delay. $T_{1\rho}$ measurements were performed as described previously using a standard $T_{1\rho}$ sequence preceded by cross

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polarization.[3] Spin lock periods of up to 20 ms were employed with ^{13}C precessional frequencies (ω_1) of around 50 kHz. Temperatures in the MAS probe were calibrated using standard samples with known phase changes run under conditions as close to those of the experimental observations as possible.[27]

Activation parameters were derived from Eyring plots of the rate data or from Arrhenius plots of $\ln(T_{1\rho})$ vs $1/T$. The theory and details of these methods are discussed in refs 3 and 5. Errors on the activation parameters quoted in this paper are 95% confidence limits estimated as twice the standard deviation calculated from least squares linear plots. Errors on the $T_{1\rho}$ values in this paper vary with the signal to noise ratio available from the sample in a reasonable time period. They would typically be around ±5%.

Synthesis of 4,4-Dimethyl-*trans*-cyclopentane-1,2-diol. This compound was prepared by standard procedures and was purified by recrystallisation from benzene to give white crystals: mp 94−95 °C (lit. 96−97 °C); δ_H (200 MHz; CDCl$_3$) 1.09 (6H, s, 2 × CH$_3$), 1.42 and 1.91 (4H, 2 × dd, CH$_2$), 2.10 (2H, s, OH), 4.08 (2H, m, CH); δ_C (50.13 MHz; CDCl$_3$), 31.98 (2 × CH$_3$), 33.72 (quat. C), 45.96 (CH$_2$), 78.85 (CH).

***trans*-Cyclopentane-1,2-diol (1) and sulfolane (2)** were purchased from Aldrich and used as received.

O−^2H derivatives of the diols were prepared by dissolving the compound in a substantial excess of ^2H_2O, leaving for an appreciable period of time (more than 1 h), then recovering the diol by evaporation. Compounds thus prepared showed no O^1H and peaks in their ^1H NMR spectra and substantial O^2H peaks in their infrared spectra.

Results and Discussion

***trans*-1,2-Cyclopentanediol (1).** Lambert *et al.*[12,13] report that this compound shows no phase transitions other than the freezing point at +55 °C. They also reported maximum dipolar broadening at ca. 263 K. Our spectra show maximum dipolar broadening at *ca.* 240 K, 23 degrees below that reported by Lambert *et al.* Lambert *et al.* indicated in their paper that they were using an uncalibrated probe/temperature controller combination. They did however show that their sample temperatures
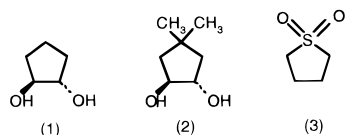
were 15−20 degrees different from the control unit setting by use of a samarium acetate sample.[28] Our probe has been carefully calibrated using known phase transitions,[27] and the calibration reproduces other known phase transitions at the correct temperatures (*vide infra*). Consistent with our temperature for maximum dipolar broadening, the $T_{1\rho}$ values also give a minimum at *ca.* 242 K for each carbon (Figure 1). Relaxation times and derived rate data are given in Table 1.

The similarity in the behavior of the $T_{1\rho}$ values for the various carbon sites could indicate that each is undergoing similar pseudoisotropic reorientation. This seems improbable from the known molecular geometry and would result in considerably deeper $T_{1\rho}$ minima.

The spectra of the O-deuterio compound were very similar to those of the O-protio compound indicating similar rates for the molecular motion. This result neither confirms nor denies that making and breaking of H-bonds is involved in the process because the line shapes of the spectra obtained would not be expected to be as sensitive to the small changes in rates of
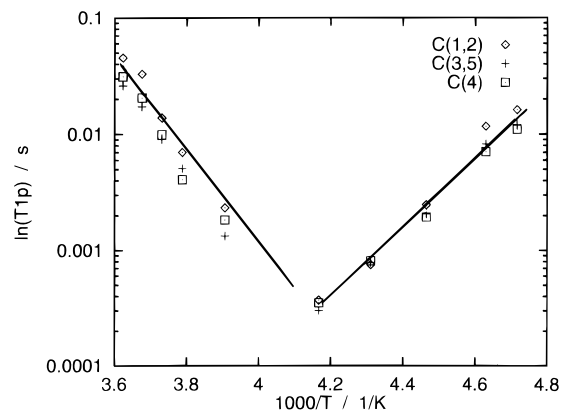
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Figure 1. The variation of $\ln(T_{1\rho})$ vs $10^3/T$ for all three carbons in *trans*-cyclopentane-1,2-diol (**1**) ($\omega_1 = 49.0$ kHz).

Table 1. $T_{1\rho}$ Values and Rates for *trans*-1,2-Cyclopentanediol (**1**) ($\omega_1 = 49.0$ kHz)[a]

	C(1,2)		C(3,5)		C(4)	
temp (K)	$T_{1\rho}$ (ms)	$k \times 10^4$ (s^{-1})	$T_{1\rho}$ (ms)	$k \times 10^4$ (s^{-1})	$T_{1\rho}$ (ms)	$k \times 10^4$ (s^{-1})
276	45.3	752	26.1	534	31.3	552
272	32.9	546	17.2	353	20.5	361
268	13.8	221	9.0	185	9.9	174
264	7.0	116	5.1	104	4.1	76.9
256	2.3	38.5	1.3	27.0	1.8	31.9
240	0.37	3.09	0.30	3.08	0.35	3.08
232	0.75	0.813	0.78	0.617	0.81	0.700
224	2.5	0.231	2.1	0.224	1.9	0.280
216	11.7	0.0488	8.3	0.0559	7.1	0.0763
212	16.2	0.0352	12.1	0.0382	11.0	0.0490

[a] [Derived values for the $^{13}C-^1H$ dipolar interaction $B^2 = 1.66 \times 10^9$ s^{-2} for C(1); 2.05×10^9 s^{-2} for C(3,5) and 1.76×10^9 for C(4)]. Note that the rate constants in this table are derived from the correlation times for molecular motions (τ_c) which is the time for the carbon atom to pass through 1 radian. The derived rates have, therefore, been corrected by a factor of 2π in order to express them in frequency units.

motion associated with isotopic exchange as those involved in coalescence phenomena.

In an attempt to determine the molecular motions occurring and their corresponding activation parameters, two models for cyclopentane were considered. The first (model 1) involved the wagging up and down of a methylene group out of the plane of the other four, to represent part of the pseudorotation process. The second (model 2) involved a reorientation of the whole molecule about a 2-fold axis passing through C(4) and bisecting the C(1)−(2) bond (C_2 reorientation). In the latter case both planar and half chair arrangements were considered.

Since the $T_{1\rho}$ relaxation times are controlled by the same correlation times and the magnitudes of $T_{1\rho}$ for C(3,5) and C(4) in compound **1** are effectively indistinguishable with C(1,2) approximately 1.5 times larger, "model 1" would at first sight appear to be the most probable with all carbons undergoing the same type of motion. As C(1,2) have only one hydrogen in close proximity it is expected that their relaxation time would be longer. That it is not twice as long is attributable to cross correlations which are present in the three spins of the methylene group and which retard the relaxation.

It has been shown that, for similar systems, cross correlations result in a relaxation describable by a sum of exponentials.[29] The decay data used to determine $T_{1\rho}$ gave no clear indication of complex relaxation. This may have been due to other interactions present which tend to reduce the cross correlation nonexponentiality. Therefore, for simplicity of calculations we

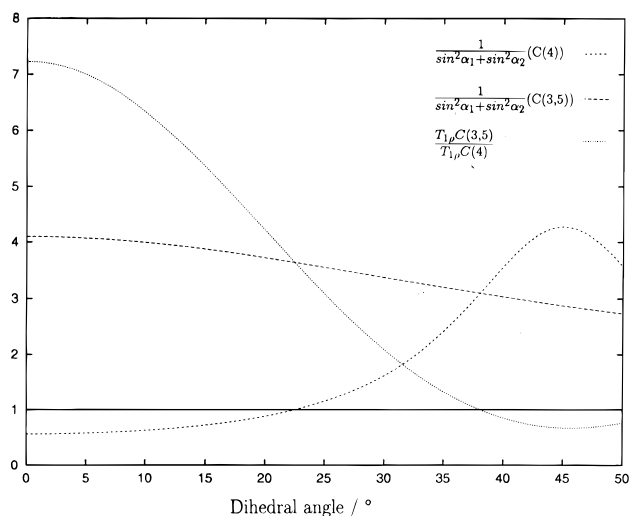(29) Hilt, R. L.; Hubbard, P. S. *Phys. Rev.* **1964**, *134A*, 393.

Figure 2. Plot of $1/(\sin^2(\alpha_1) + \sin^2(\alpha_2))$ vs puckering angle for C(3,5) and C(4) for model 2.

considered only the effects of autocorrelations, the independent correlations of single internuclear vectors with themselves at a later time.

The wagging of the methylene group was modeled by a two site jump model between maximum puckering on either side of the plane of the other four. Extending the work of O'Reilly *et al.*,[30] it is easily shown that the relaxation time will take the following form

$$T_{1\rho}^{-1} = \gamma_I^2 \gamma_S^2 \mathbf{h}^2 \left(\frac{\mu_o}{4\pi}\right)^2 r^{-6} (\sin^2(\alpha_1) + \sin^2(\alpha_2)) \frac{9}{40} \times$$

$$\left\{ \frac{3}{2}\left[\frac{\tau}{1 + \omega_I^2\tau^2}\right] + \frac{1}{6}\left[\frac{\tau}{1 + (\omega_I - \omega_S)^2\tau^2}\right] + \right.$$

$$\left. \frac{1}{2}\left[\frac{\tau}{1 + \omega_I^2\tau^2}\right] + \left[\frac{\tau}{1 + \omega_S^2\tau^2}\right] + \left[\frac{\tau}{1 + (\omega_I + \omega_S)^2\tau^2}\right]\right\}$$

where α_i is the angle through which CH_i jumps.

This equation can be applied to both models. Clearly for model 1 all CH vectors will undergo the same change of angle, resulting in the same relaxation times for C(3,5) and C(4) as was observed. Figure 2 shows a plot of "$1/(\sin^2(\alpha_1) + \sin^2(\alpha_2))$ vs puckering angle" for C(3,5) and C(4) for "model 2". This represents how how $T_{1\rho}$ changes with the puckering angle at any given temperature. Also plotted is the ratio of these two

$$\frac{T_{1\rho}(C(3,5))}{T_{1\rho}(C(4))}$$

For angles up to ~35° model 2 is incompatible with the experimental data. The puckering angle for envelope (C_s) cyclopentane in free molecules in the gas phase has been found to be about 35°, and the dihedral angle in twist (C_2) cyclopentane has been calculated to be 21°.[18] Both angles would be expected to be less in a substituted derivative. The incorporation of the molecules in a solid would also be expected to reduce the maximum puckering and dihedral angles. Moreover, the wagging model for the pseudorotation (model 1) probably exaggerates the extent of the molecular motion in a true pseudorotation process which is a smooth transition between C_2 and C_s conformations not a jumping motion between C_s conformations.

Although C_2 reorientation cannot be entirely ruled out, model 1, a flapping model for the pseudorotation process, would appear to be the more likely on the basis of the equality of the $T_{1\rho}$ values at C(3,5) and C(4) and the calculations described above and, therefore, pseudorotation of the five-membered ring the more likely origin of our observations.

The strength of the dipolar interactions (B^2) were obtained from the experimentally determined $T_{1\rho}$ minima and the precessional frequency of ^{13}C in the spin locking field. These values then allowed calculation of the correlation time for the molecular motion which is closely related to the mean time between changes in the molecular conformation. The derived rates, expressed in frequency units, are the inverse of the correlation times.

The values of B^2 obtained are an order of magnitude greater than those we have obtained earlier for the carbons in the methyls of a *tert*-butyl group as it reorients about its local 3-fold axis. This reflects the fact that depth of the modulation of the residual dipolar interaction in the *tert*-butyl group is much less than for the case discussed here.

The rates reported by each of the carbon atoms are very similar and suggest that they are all subject to the same motion. Accordingly, for calculation of the energy of activation, the average rate at each temperature was used. The rates of the molecular motion are seen to vary quite rapidly with temperature, and they give an energy of activation of 77 kJ·mol^{-1}. The above data are entirely compatible with the pseudorotation of the five-membered ring in which each carbon is subject to a similar degree and rate of motion. The magnitude of the activation energy is comparable to that for other hydrogen bond exchange processes we have measured[31] suggesting that hydrogen bonds are being made and broken during the pseudorotation process.

4,4-Dimethyl-*trans*-1,2-cyclopentanediol (2). To complement the studies on *trans*-1,2-cyclopentanediol we prepared and examined 4,4-dimethyl-*trans*-1,2-cyclopentanediol. The temperature variation of its ^{13}C CP/MAS spectra are shown in Figure 3. At low temperatures two resonances are observed for the methylene carbons (C(3,5)) (ca. 45 ppm) and four (one is a shoulder at 284 K) for the methyls (C(6,6′)) (ca. 35 ppm) whilst C(1,2) (ca. 76 ppm) and C(4) (32 ppm) appear as singlets. There are coalescences of the C(3,5) and methyl resonances for which the data are presented in Table 2. The average free energy of activation for these coalescences is ca. 58 kJ·mol^{-1} at ca. 301 K. Coalescence temperatures were also recorded for the O-deuteriated derivative (Table 2) and were ca. 6 K higher giving an average free energy of activation for the process of 59 kJ·mol^{-1} at 307 K. This increase in coalescence temperature and free energy of activation is consistent with a hydrogen bond exchange being involved in the observed process. We consider these differences to be reliable as line shape changes around coalescence, including these, are reproducible in our hands provided that appropriate precautions are taken.[27]

All the resonances showed signs of maximum dipolar broadening at temperatures above the coalescence, and so $T_{1\rho}$ values were determined in an attempt to extend the temperature range of the rate measurements. The resulting $T_{1\rho}$ values between ambient temperature and 342 K are given in Table 3 and plotted in Figure 4. Data were not recorded above 342 K because of the approaching melting point (367 K) and the deteriorating signal to noise ratio. No $T_{1\rho}$ minimum was reached.

This set of data contrast markedly with that of **1**. The different carbon atoms show substantially different values for

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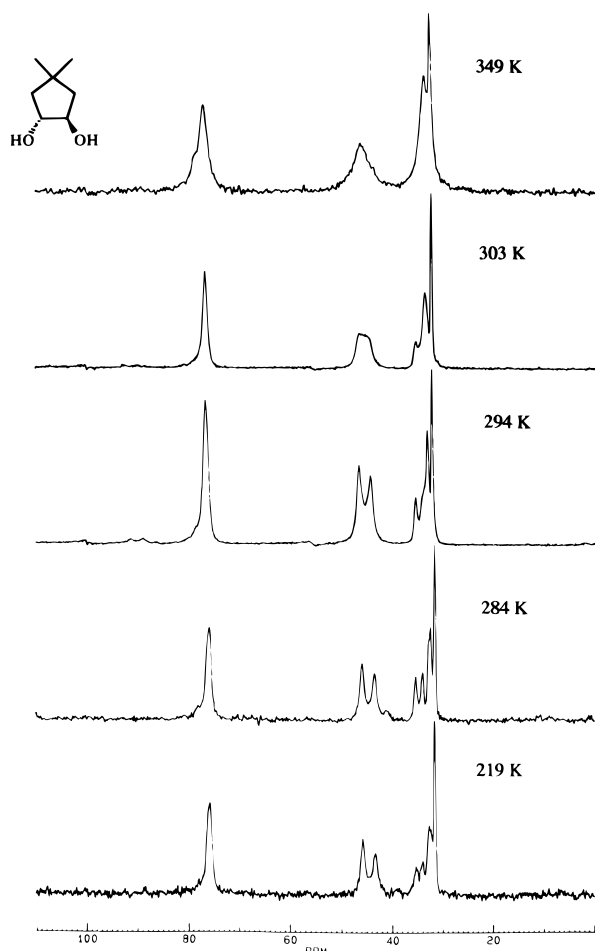(31) Cameron, K. S.; Riddell, F. G.; Spark, R. A. Unpublished results.

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Figure 3. ^{13}C CP/MAS NMR spectra of 4,4-dimethyl-*trans*-cyclo-pentane-1,2-diol (**2**).

Table 2. Data and $\Delta G^{\ddagger}_c$ Values for 4,4-Dimethyl-*trans*-1,2-cyclopentanediol (**2**)

	O$-^1$H			O$-^2$H		
carbon	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}_c$ (kJ mol^{-1})	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}_c$ (kJ mol^{-1})
3,5	303	288	58.3	308	292	59.1
6	294	172	57.0	298	143	58.7
6′	306	356	58.4	315	311	60.1

Table 3. $T_{1\rho}$ Values (ms) for the Four Resonances in 4,4-Dimethyl-*trans*-1,2-cyclopentanediol (**2**) ($\omega_1 = 42.2$ kHz)

temp (K)	C(1,2)	C(3,5)	C(4)	C(6,6′)
342	1.1	5.7	3.9	
335	1.4	0.62	6.7	5.3
328	2.2	0.85	9.4	6.3
320	3.8	0.85	13.8	8.8
313	4.0	1.6	16.9	9.7
306	4.5	1.7	20.5	13.5
299	5.0	2.5	21.6	16.9
293	5.4	2.0	26.3	20.0

their relaxation times. This is unremarkable for C(4), a quaternary carbon with no directly bound hydrogens. However, the contrast in the values for C(1,2) and C(3,5) with that for the methyl groups C(6,6′) strongly indicates that the molecular motion on which these measurements are reporting is centered on carbons 3 and 5 with substantial effects on carbons 1 and 2. The $T_{1\rho}$ minimum for C(3,5) is certainly less than 0.6 ms and so is in line with our results described above for a wagging motion, most probably a pseudorotation in which perhaps the largest amplitude is centered on C(3,5).
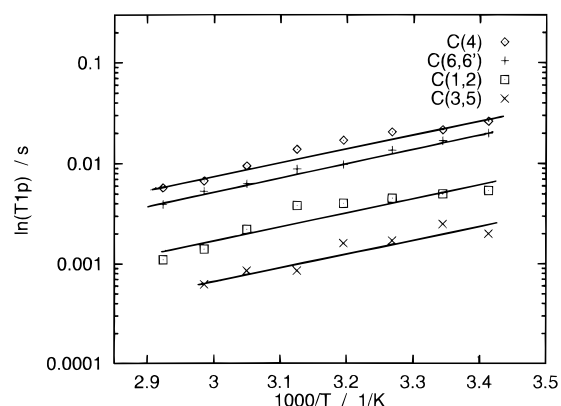

Figure 4. Temperature variation of $T_{1\rho}$ for all four carbons in 4,4-dimethyl-*trans*-cyclopentane-1,2-diol (**2**) ($\omega_1 = 42.2$ kHz).

Even more remarkable is the fact that the energies of activation (ca. 26.5 kJ·mol^{-1}) derived from the $T_{1\rho}$ values are very much lower than the free energy of activation from the coalescence process. It must be that the $T_{1\rho}$ values are reporting on a different motion from the coalescence. It is conceivable that the coalescence arises from a hydrogen bond exchange process that does not involve substantial molecular motions and so does not contribute appreciably to $T_{1\rho}$ relaxation. The $T_{1\rho}$ values, on the other hand, must then be reporting on a different dynamic process, most probably a ring pseudorotation in which the largest amplitude of motion is centered on carbons 1, 2, 3, and 5.

In both **1** and **2** there is evidence of hydrogen bond exchange processes. Other work that we have carried out on low molecular weight 1,3-diols also points to the existence of dynamic hydrogen bond processes in some of these systems. Dynamic hydrogen bond exchange in the solid state, therefore, seems to be a fairly general phenomenon in small molecules containing hydroxyl groups.

Sulfolane (3). The final compound on which we report is sulfolane which was previously studied by Lambert *et al.*[12,13] who observed maximum dipolar broadening. Observations on sulfolane are complicated by its phase behavior. There are four phases reported for this compound.[32] There are two plastic crystalline phases: I between the MP at 301 K and 296 K and II between 296 K and 288 K. There are also two brittle crystalline phases reported, III between 288 K and 246 K and IV below 246 K. Phase II has been studied by X-ray diffraction and shows that there is disorder caused by rapid molecular rotation.[33] The phase transition III → IV was reported by Kydon *et al.*[32] to show only a very small change in ^{1}H $T_{1\rho}$ values. Because of the larger errors in our ^{13}C $T_{1\rho}$ measurements we were unsure whether the phase change III → IV would be visible using our methods. The plastic phases of sulfolane have previously been studied by ^{1}H and ^{2}H NMR.[34] We note that Lambert *et al.* gave the plastic to crystalline phase transition at 288 K a free energy of activation mistaking it for a coalescence. This is clearly inappropriate for a phase transition.

The spectra we obtained are similar to those obtained by Lambert *et al.* with the exception of the recorded temperatures. The spectrum at 296 K contains relatively sharp lines and is consistent with a plastic crystalline phase. Immediately below the plastic to brittle crystalline transition each carbon resonance is doubled as was observed by Lambert. Maximum dipolar

(32) Kydon, D. W.; Sharp, A. R.; Hale, M. E.; Watton, A. *J. Chem. Phys.* **1980,** *72,* 6153.
(33) Immirzi, A.; Jannelli, L. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 39.
(34) Akimov, M. N.; Bezrukof, O. F.; Struts, A. V.; Ustimov, V. I. *J. Struct., Chem.* **1989**, *30*, 906.

Table 4. $T_{1\rho}$ Values (ms) and Rates (s^{-1}) for the Two Resonances in Sulfolane (**3**) ($\omega_1 = 51.4$ kHz)

	C(1)		C(2)	
temp (K)	$T_{1\rho}$	$k \times 10^5$	$T_{1\rho}$	$k \times 10^5$
288	24.5	330	17.5	305
280	14.2	191	15.6	272
272	11.8	159	7.8	137
264	8.7	89.3	4.6	79.4
256	4.9	65.8	3.2	55.2
248	0.82	10.0	0.80	13.2
240	0.65	7.35		
224	2.1	0.37	0.80	0.79
216	2.7	0.29	3.5	0.17
208	7.2	0.11	6.2	0.096
204	8.8	0.089	6.5	0.092

[a] These data give values for the $^{13}C-^{1}H$ dipolar interactions (B^2) of 1.35×10^9 s^{-2} (C(1)) and 1.74×10^9 s^{-2} (C(2)). The average values of the rate constants give an energy of activation of 52.3 ± 2.1 kJ·mol^{-1}. Note that the rate constants in this table are derived from the correlation times for molecular motions (τ_c) which is the time for the carbon atom to pass through 1 radian. The derived rates have, therefore, been corrected by a factor of 2π in order to express them in frequency units.
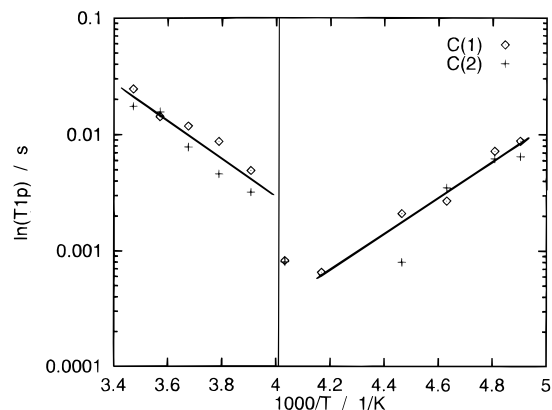
Figure 5. The variation of $\ln(T_{1\rho})$ vs $10^3/T$ for both carbons in sulfolane (**3**) ($\omega_1 = 51.4$ kHz). The discontinuity below ca. $10^3/T = 4.0$ (ca. 250 K) is probably due to the phase change III → IV known to occur at 246 K.

broadening occurs at around 240 K, but the lines do not resolve as was observed by Lambert *et al.* even down to 204 K probably because a lower temperature is required for this to happen. The doubling may arise either from nonequivalence of the carbons 2 and 5 due to dissymetry in the solid or from two independent molecules in the asymmetric unit.

$T_{1\rho}$ measurements were made and are reported in Table 4. Although there appears to be no evidence of a phase change at 246 K either in the chemical shift values or in discontinuities in the $T_{1\rho}$ values, a logarithmic plot of $T_{1\rho}$ vs $1/T$ (Figure 5) reveals a slight discontinuity in that the linear left hand side

portion intersects the linear right hand side portion above the minimum point in the graph. Moreover, this seems to occur at around the correct temperature (246 K) confirming the existence of the change. The structural changes at the phase transition temperature must be small to give rise to such small changes in chemical shift and $T_{1\rho}$ values. The $T_{1\rho}$ values for both resonances are very similar indicating that both carbons are subject to a similar degree of molecular motion. On the basis of our calculations and observations described above the minimum values for $T_{1\rho}$ (between 0.65 and 0.8 ms) are consistent with those expected for the reorientation of the molecules about their local C_2 axes.

The assignment of a molecular reorientation as the origin of the ^{13}C CP/MAS measurements is in agreement with the earlier work of Kydon *et al.*[31] The energy of activation derived from the frequencies of the molecular motions and ignoring the phase change is 52.3 ± 2.1 kJ·mol^{-1}, almost identical to that reported by Kydon *et al.* for whole molecule C_2 reorientation in phase III. This value is substantially greater than the activation energy for pseudorotation partitioned out for **2** strengthening the suggestion that it arises from a whole molecule rotation process. However, this conclusion should be treated with some caution because the observations may arise from two independent molecular species, and we have ignored the small phase change that occurred during the course of our measurements.

Conclusions

The results for the *trans*-1,2-cyclopentanediols strongly indicate that pseudorotation processes are occurring in the solid phase with differing activation energies and also provide strong evidence that there are dynamic hydrogen bond exchange processes occurring in these compounds. The nature of the process in supholane is probably a molecular reorientation about an internal C_2 axis of the molecule, but pseudorotation cannot be entirely ruled out because of associated ambiguities. The activation energy for the dynamic hydrogen bond exchange processes observed in the solid state in these compounds is around $50-60$ kJ·mol^{-1}. If, as seems to be the case, the activation energy for ring pseudorotation in **2** is ca. 30 kJ·mol^{-1}, then the observed activation energy for compound **1** 77 kJ·mol^{-1} is seen to be approximately the sum of the activation energies for pseudorotation and hydrogen bond exchange helping to confirm the origin of the process. Isotopic exchange of ^{2}H$-$O for ^{1}H$-$O in crystalline alcohols can lead to alterations in the rates of hydrogen bond exchange processes and is potentially a useful method for identifying these processes in solids particularly where the lineshape is sensitive to small rate changes.