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# Dynamics of Five-Membered Rings in the Solid State by NMR Spectroscopy

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**Abstract:** The carbon-13 NMR spectra have been investigated in the solid state for a number of fundamental five-membered rings and some analogous six-membered rings. Several of these rings freeze into a plastic phase, whose NMR spectrum retains the symmetry of the liquid-phase spectrum. At the plastic-to-nonplastic transition, these spectra can undergo decoalescence to spectra characteristic of the symmetry and structure within the solid. Motion within the solid also broadens peaks when the motional frequency is comparable to the spin-lock precessional frequency. In the nonplastic phase, cyclopentanol exists in at least two sites, and possibly more, which probably result from hydrogen-bonded aggregation. Cyclohexanol may exist in two such sites. Cyclopentanone exists in two equally populated sites. 1-Methylcyclopentanol and *trans*-1,2-cyclohexanediol exist either in two equally populated sites or as a single, unsymmetrical form. Cyclohexanone, *trans*-1,2-cyclopentanediol, and tetrahydrothiophene 1-oxide appear to exist in single forms. Sulfolane exists in two, unequally populated sites.

When compared with six-membered rings, five-membered rings are conformationally far more complex. The envelope and half-chair (or twist) conformations of five-membered rings possess three different positions on the ring, from which substituents may be attached at a total of 11 different locations. Moreover, these ring positions and substituent locations are in rapid equilibrium through pseudorotation, as shown first by Kilpatrick, Pitzer, and Spitzer to explain the high gas phase entropy of cyclopentane[1] and corroborated later by other forms of spectroscopy.[2–7] The equilibration of forms is rapid on the NMR time scale,[6] so that the dynamic methods of NMR have not been able to be applied to five-membered rings in solution.

Although the conformational reorientation of groups within a molecule often occurs at similar rates in solution and in the solid, conformational processes can have much higher activation energies in the solid because of lattice constraints and because new interactions may exist in the solid that were not present in solution.[8–10] For this reason, we initiated a program to examine the NMR spectra of common five-membered rings using standard cross polarization and magic angle spinning (CP/MAS) procedures in order to obtain high-resolution spectra. Numerous investigations have been reported of conformational and other dynamic processes in the solid by CP/MAS techniques,[10,11] but not, to our knowledge, of the conformational properties of five-membered rings.[12] Dynamic solid-state NMR spectroscopy also has been used to study transitions between solid phases.[13,14] One impediment to studying five-membered rings by dynamic solid-state techniques is the simple fact that most such simple rings are liquids at room temperature. These materials, however, may be introduced into the rotor as liquids, and the temperature of the system may then be lowered to below the freezing point.[12,15] The process of lowering the temperature permits examination first of effects on the spectrum at the phase transition to freezing and then of other effects that occur only in the solid phase(s).

In the present study we have applied the $^{13}$C CP/MAS NMR method to a variety of simple and important five-membered rings. It is noteworthy that no crystal structure has been reported for any of our molecular subjects, although many of them were examined crystallographically. Poor low-temperature capabilities, disorder in the solid, the presence of multiple forms, and phase transitions that alter the crystals probably contributed to such negative results. Thus what structural information as may be obtained by solid-state NMR spectroscopy would be unique.

## Results

Prior to each NMR experiment, differential scanning calorimetry (DSC) was used to locate phase transitions within the temperature range under consideration (−100 to +100 °C). For our purposes, DSC was used primarily to locate phase transition temperatures that were not available in the literature.

**Cyclopentanol.** The DSC thermogram shows phase transitions at −19 (the melting point), −37, and −73 °C. The $^{13}$C spectrum at room temperature of the liquid contains three peaks at $\delta$ 24 (C3), 36 (C2), and 74 (C1). All three peaks broaden as the temperature is lowered and the sample is allowed to freeze (Figure

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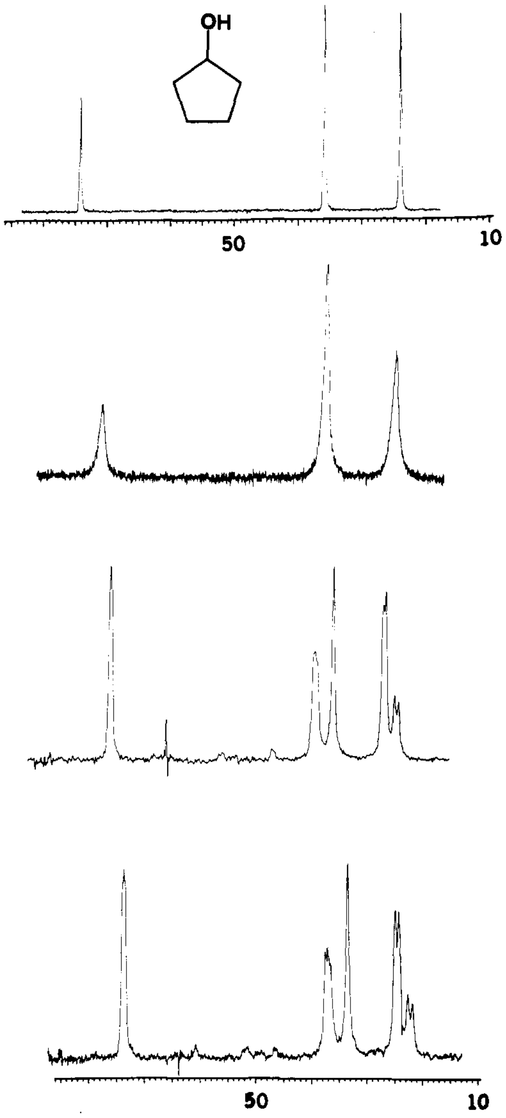

**Figure 1.** Carbon-13 CP/MAS spectra of cyclopentanol (from top) at -25, -55, -70, and -80 °C.

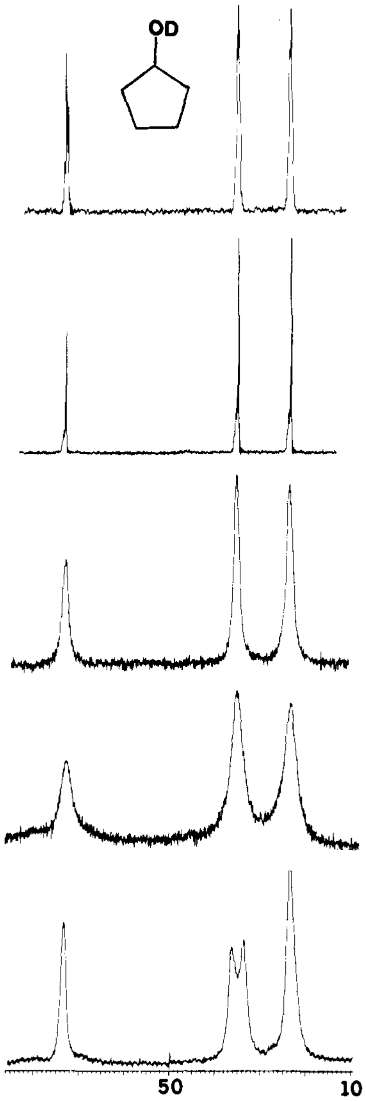

**Figure 2.** Carbon-13 CP/MAS spectra of cyclopentanol-*OD* (from top) at +27, -20, -60, -80, and -90 °C.

1). The temperature measured by the console, as pointed out in the Experimental Section, is about 20 °C higher than the actual temperature, but we shall specify the temperature as calibrated with samarium acetate tetrahydrate, probably to an accuracy of only ±5 °C. Between the melting point and about -55 °C, the peaks slowly broaden. Within this region, *the use of cross polarization does not aid in improving the quality of the spectrum.* Such an observation with solids often is indicative of rapid motion within the lattice. Between -55 and -70 °C, broadening and decoalescence occur. The resonance of C1 splits into two peaks and that of C2 and C3 splits into three or four peaks. Below -80 °C, further splitting into at least eight peaks occurs for the two higher field resonances, and the relative proportions of the peaks change significantly.[12] All these changes are entirely reversible, and there are no spinning sidebands at any temperature.

**Cyclopentanol-*OD*.** The $^{13}$C spectrum of the OD derivative closely resembles that of the parent OH species, but changes occur at correspondingly lower temperatures (Figure 2). The peaks do not broaden until about -60 °C, and narrowing after decoalescence does not occur until -90 °C. Cross polarization does not improve the spectrum until below decoalescence.

**Cyclohexanol.** The room-temperature $^{13}$C spectrum contains the four expected peaks at $\delta$ 25 (C3), 26 (C4), 35 (C2), and 70 (C1). Although the melting point is +22 °C, supercooled liquid may still be present for the 0 °C spectrum (Figure 3). For the remaining illustrated spectra, however, it was clear from the response to cross polarization that the sample had solidified. DSC experiments show complex phase behavior that is extremely sensitive to the thermal history of the sample.[16] Between 0 and -80 °C, all the $^{13}$C peaks broaden and then narrow again without decoalescence into additional peaks. At -80 °C, the spectrum closely resembles a broadened version of the room-temperature spectrum. Between -80 and -100 °C decoalescence occurs only in the peak at $\delta$ 35, which splits into two.

**Cyclopentanone.** At room temperature there are peaks at $\delta$ 25 (C3), 39 (C2), and 220 (C1). Cyclopentanone melts at -51 °C, but no change occurs in the spectrum to -70 °C (Figure 4). This phenomenon of supercooling also was observed in the DSC thermogram. Solidification occurs by -80 °C and is immediately evident by the improvement provided by cross polarization and the appearance of spinning sidebands around the carbonyl resonance. Moreover, the C1 (carbonyl) and C2 peaks are split into two. This behavior contrasts with that of cyclopentanol, which does not decoalesce until some 50 °C below freezing. Line widths are quite narrow to -100 °C. The DSC thermogram shows no transition other than melting or freezing.

**Cyclohexanone.** At room temperature there are resonances at $\delta$ 25 (C4), 27 (C3), 43 (C2), and 211 (C1). The freezing point is -47 °C, and this phase change is immediately evident in the spectrum by the improvement provided by cross polarization and the appearance of the carbonyl spinning sidebands (Figure 5).

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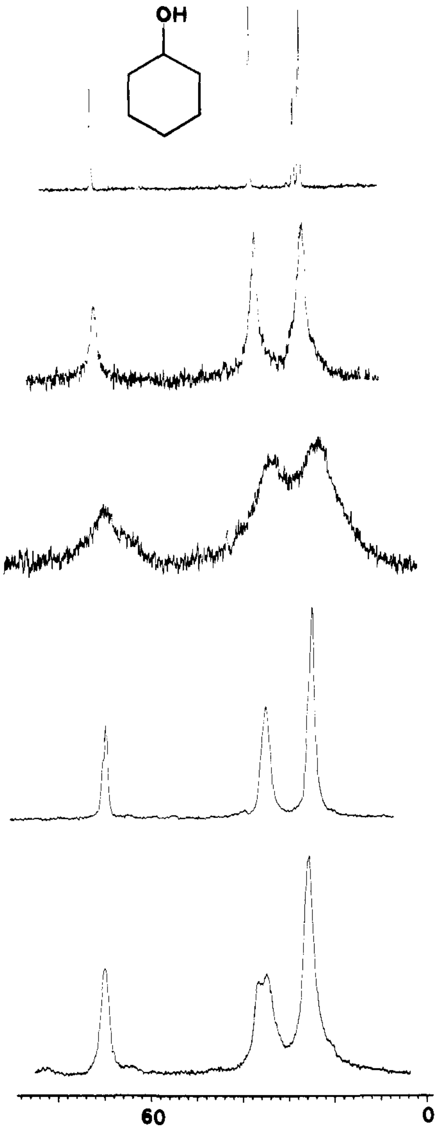

**Figure 3.** Carbon-13 CP/MAS spectra of cyclohexanol (from top) at 0, −40, −70, −80, and −100 °C.

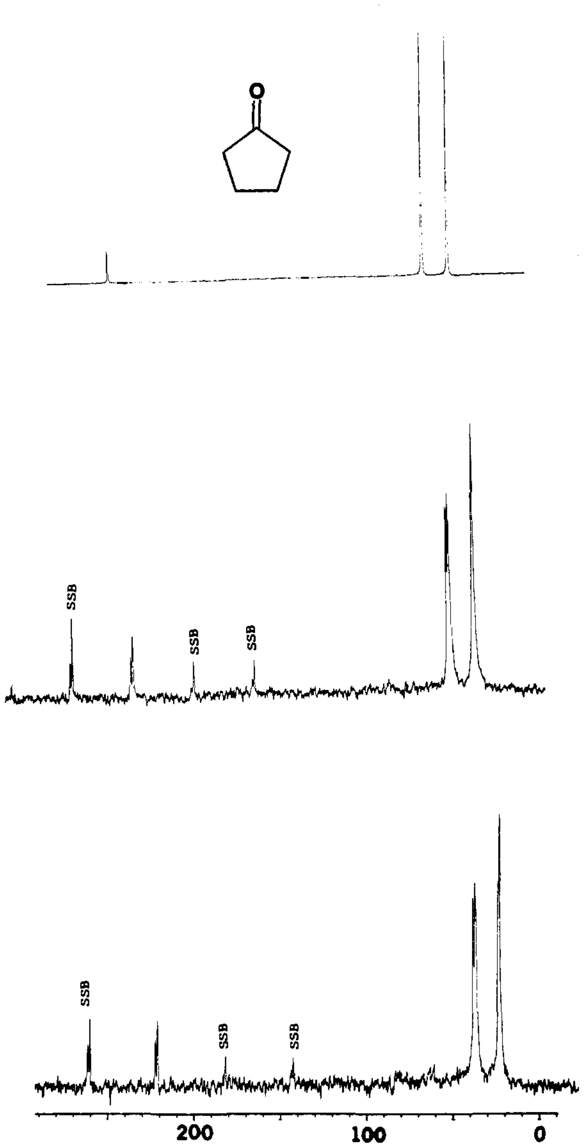

**Figure 4.** Carbon-13 CP/MAS spectra of cyclopentanone (from top) at −70, −90, and −100 °C.

The upfield peaks broaden slightly at −55 °C and narrow again by −70 °C. All four peaks are still visible, and no further splitting is observed.

**1-Methylcyclopentanol.** The DSC thermogram shows no transitions other than the freezing point at +37 °C. The $^{13}$C spectrum of the liquid shows the expected four peaks at $\delta$ 26 (C3), 30 (Me), 43 (C2), and 81 (C1) (Figure 6). Slight broadening occurs with freezing. There is possible splitting of the C2 resonance at −80 °C.

***trans*-1,2-Cyclopentanediol.** The DSC thermogram shows no transitions other than the freezing point at +55 °C. At room temperature, the $^{13}$C spectrum of the solid contains three peaks, $\delta$ 19 (C4), 30 (C3), and 77 (C1), which broaden enormously as the temperature is lowered (Figure 7). Resharpening occurs below −10 °C without peak splitting. Throughout the temperature range to −80 °C cross polarization does not improve the spectrum.

***trans*-1,2-Cyclohexanediol.** The DSC thermogram shows no transitions other than the freezing point at +100 °C. The sample was melted, and the $^{13}$C spectrum was recorded with cooling in the same manner as for the other samples (Figure 8). There are three peaks at +100 °C, $\delta$ 24 (C4), 33 (C3), and 75 (C1). Some broadening occurs below freezing, and all peaks split into two by +30 °C. There are no further changes to −80 °C.

**Sulfolane.** This material, $(CH_2)_4SO_2$, melts at +27 °C, undergoes a phase transition at +15 °C, and may have another phase transition at −63 °C.[17] At room temperature, the $^{13}$C NMR spectrum contains the expected pair of peaks at $\delta$ 23 (C2) and 52 (C1), which decoalesce quickly into two peaks each (Figure 9, −5 °C). Considerable broadening occurs between −10 and −55 °C, and the spectrum resharpens at about −75 °C. At −80 °C, the spectrum closely resembles the pair of doublets at −5 °C, except that the relative intensities have changed. Cross polarization gives no improvement until below −70 °C.

**Tetrahydrothiophene 1-Oxide.** The DSC thermogram shows no transitions other than freezing at −38 °C. The $^{13}$C spectrum remains a pair of sharp peaks, $\delta$ 26 (C2) and 55 (C1), down to −85 °C (Figure 10).

Spectra were recorded for numerous other five-membered rings, including tetrahydrofuran, methoxy- and ethoxycyclopentane, methoxy- and ethoxycyclohexane, *tert*-butoxycyclohexane, dicyclopentylamine, cyclopentyl mercaptan, (trimethylsiloxy)-cyclopentane, dicyclopentyl ether, dicyclohexyl ether, cyclopentyl phenyl ether, cyclohexyl cyclopentyl ether, cyclopentylphenylamine, and tetrahydrothiophene, but these materials failed to freeze within the temperature range of observation.

For those samples that underwent decoalescence, a rate constant at coalescence was calculated from the formula $k_c = \pi\Delta\nu/1.414$, in which $\Delta\nu$ is the peak splitting in hertz.[18] The free energy of

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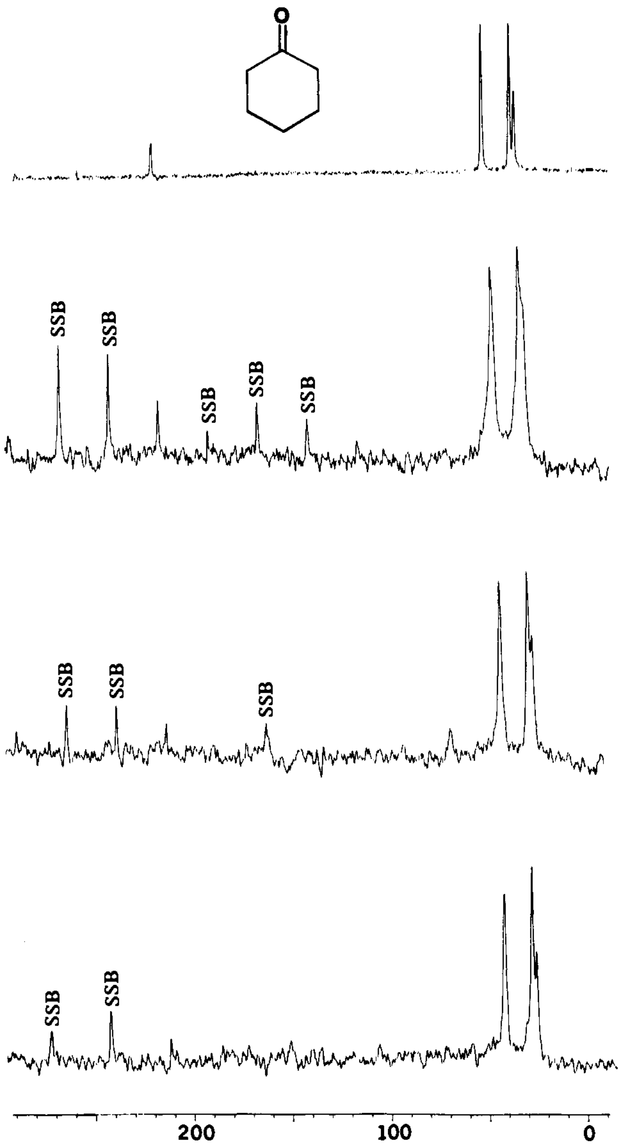

**Figure 5.** Carbon-13 CP/MAS spectra of cyclohexanone (from top) at 0, -55, -70, and -80 °C.

activation at coalescence was calculated from this rate constant, $\Delta G_c^{\ddagger} = 4.57T_c\,(10.32 + \log(T_c/k_c))$ (Table 1).

## Discussion

**Cyclopentanol.** No changes occur in the CP/MAS $^{13}$C NMR spectrum until some 50 °C below the freezing point. This observation is not time dependent, as changes do not occur even if cyclopentanol is held just below freezing for hours. Between its freezing point at -19 °C and the phase transition at -73 °C, cyclopentanol exists as a plastic solid. The plastic or rotatory phase was first described by Timmermans in 1961[19] and often occurs with molecules that may be termed globular in shape, that is, they have a center of symmetry or they are equivalent to a sphere through rapid rotation about an axis within the solid. Molecules within a plastic phase remain in a defined lattice position but rotate rapidly at that position. Such behavior has a number of ramifications, including giving rise to a high melting (freezing) point with a low entropy of transition (<5 cal mol$^{-1}$ K$^{-1}$). Below the freezing point there is a transition from the plastic phase to the nonplastic solid, which occurs with a higher entropy. Between the freezing point and the plastic-to-nonplastic transition, the molecule maintains its rotational freedom. Because all reorientations within the solid are not equally favorable, intermediate transitions can occur, as with cyclopentanol at -37 °C. The rapid in-place motion of molecules in plastic crystals means that longitudinal relaxation can be much faster than in static (nonplastic) solids, so liquid-like spectra are obtained. It is for this reason that cross polarization often had no effect on the spectra of some of the five-membered rings in this study.

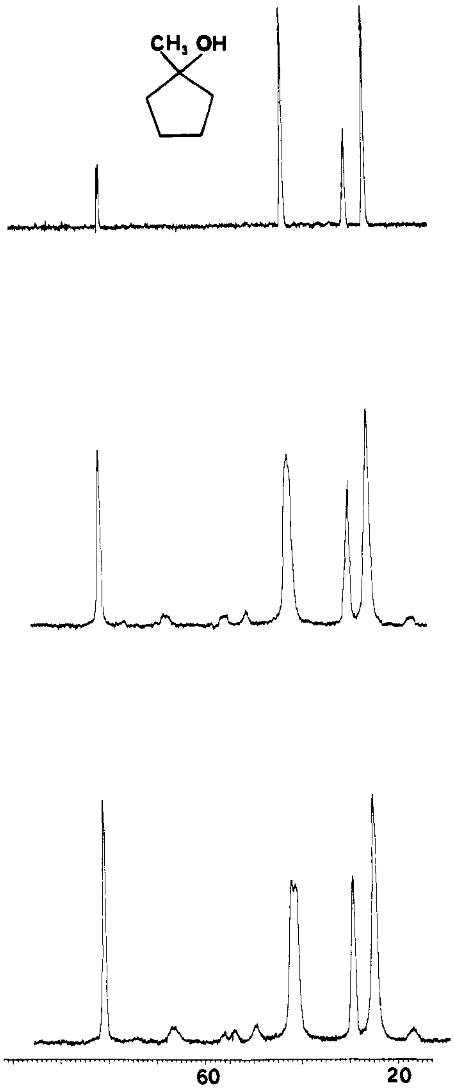

**Figure 6.** Carbon-13 CP/MAS spectra of 1-methylcyclopentanol (from top) at +40, 10, and -80 °C.

The crystal structure of cyclopentanol was attempted by Green and Wheeler in 1969, but they obtained only limited unit cell information.[20] They proposed a closely packed hexagonal structure between -19 and -37 °C, in which the molecules rotate with spherical symmetry on the average. They suggested that between -37 and -73 °C the molecules retain the same positions but with reduced orientational freedom. The transition at -73 °C disrupts the structure in the solid to such an extent that no further X-ray information could be obtained.[21]

Plastic crystals also exhibit changes in the dielectric constant with temperature. Whereas the dielectric constant normally falls at the freezing point, for many plastic crystals it rises.[19] By application of the Onsager equation, Green and co-workers[21] estimated that for cyclopentanol there are three molecules associated through hydrogen bonds in both plastic forms between -19 and -73 °C. In the higher temperature form, there is virtually no restriction to reorientation, including changes of hydrogen-bonded partners, whereas between -37 and -73 °C there is reduced orientational freedom.

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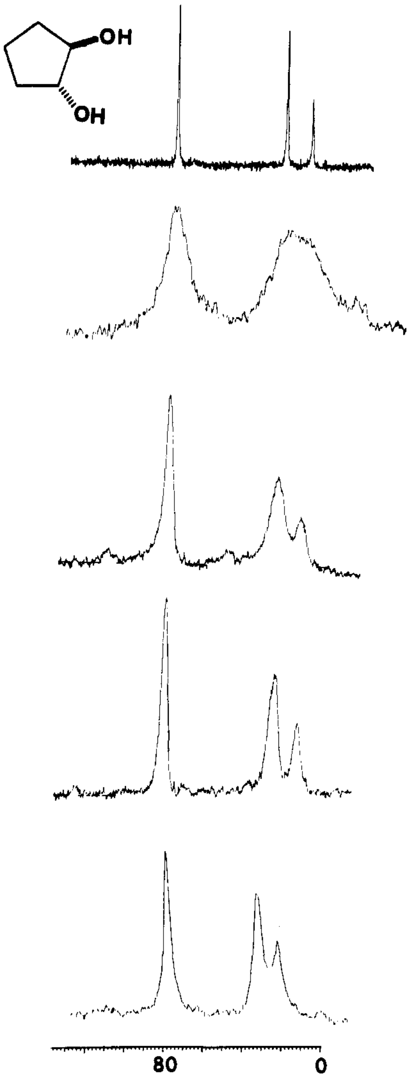


**Figure 7.** Carbon-13 CP/MAS spectra of *trans*-1,2-cyclopentanediol (from top) at +31, 0, -20, -40, and -60 °C.

The $^{13}C$ spectrum of cyclopentanol (Figure 1) now may be interpreted in terms of its plastic phases. The freezing point and the transition at -37 °C are almost invisible to the NMR experiment because of rapid in-place molecular rotation in the plastic solid. At the plastic-to-nonplastic transition at -73 °C, reorientation becomes slow on the NMR time scale, and the spectrum finally reflects the actual structure in the solid. By this point (see the -70 °C spectrum in Figure 1; temperatures are ±5 °C), there are at least two C1 sites and four C2 and C3 sites. As any single molecule can have no more than one C1 and two C2 and C3 sites, the spectrum suggests at least two distinct molecules. The intensities indicate that the lower field C2 resonances ("LC2") are associated with the higher field C3 resonances ("HC3") (C2 is lower field than C3) and that the higher field C2 resonances ("HC2") are associated with the lower field C3 resonances ("LC3"). Moreover, as the temperature is lowered, the relative intensities of the peaks change, so that the HC2/LC3 form clearly moves from being more intense than the LC2/HC3 form to being less intense.[12] Moreover, below -100 °C both of these forms further split into more peaks (up to eight each for C2 and C3). These low-temperature changes were illustrated earlier.[12]

We cannot define the structures of these forms, but we can enumerate several possibilities. (1) Conformational families: The half-chair and envelope forms could give distinct resonances, although their rapid interconversion is more likely. (2) Positional isomers: The hydroxy group can be attached to three different positions on either the half-chair or the envelope form. If it is off the symmetry plane of the envelope or off the $C_2$ axis of the half-chair form, the molecule contains two different C2 and C3 carbons, which, however, can interconvert by pseudorotation. This possibility is particularly viable below -100 °C. (3) Axial and equatorial ("geminal") isomers: The hydroxy group can exist in two different positions on each carbon in the envelope form and on both off-axis positions of the half-chair form. Pseudorotation should interconvert these forms, as it does with the conformational families, but we cannot eliminate the possibility. (4) Slow rotation about the C–O bond: The OH group then favors a single side of the ring, again giving rise to two distinct C2 and C3 carbons (**1**). The result in the NMR spectrum is identical to case (2).

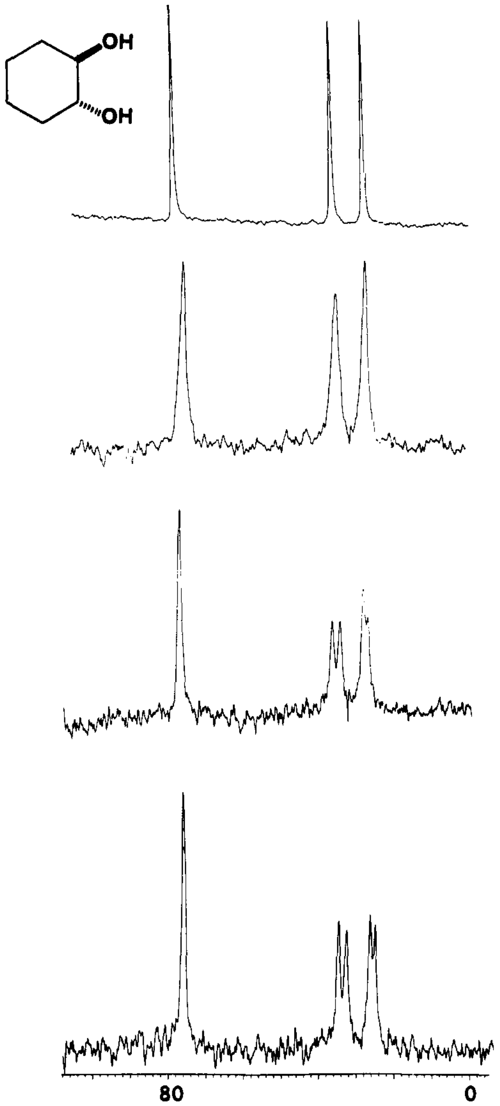
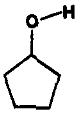
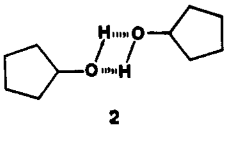


**Figure 8.** Carbon-13 CP/MAS spectra of *trans*-1,2-cyclohexanediol (from top) at +100, +55, +38, and -80 °C.



**1**

(5) Hydrogen-bonded aggregates: Not only might dimers be different from trimers, but the molecules within trimers and higher oligomers are nonequivalent. Moreover, even within a dimer, hydrogen bonding should distinguish the two sides of a molecule, so that there are two different C2 and C3 carbons (**2**). (6) In



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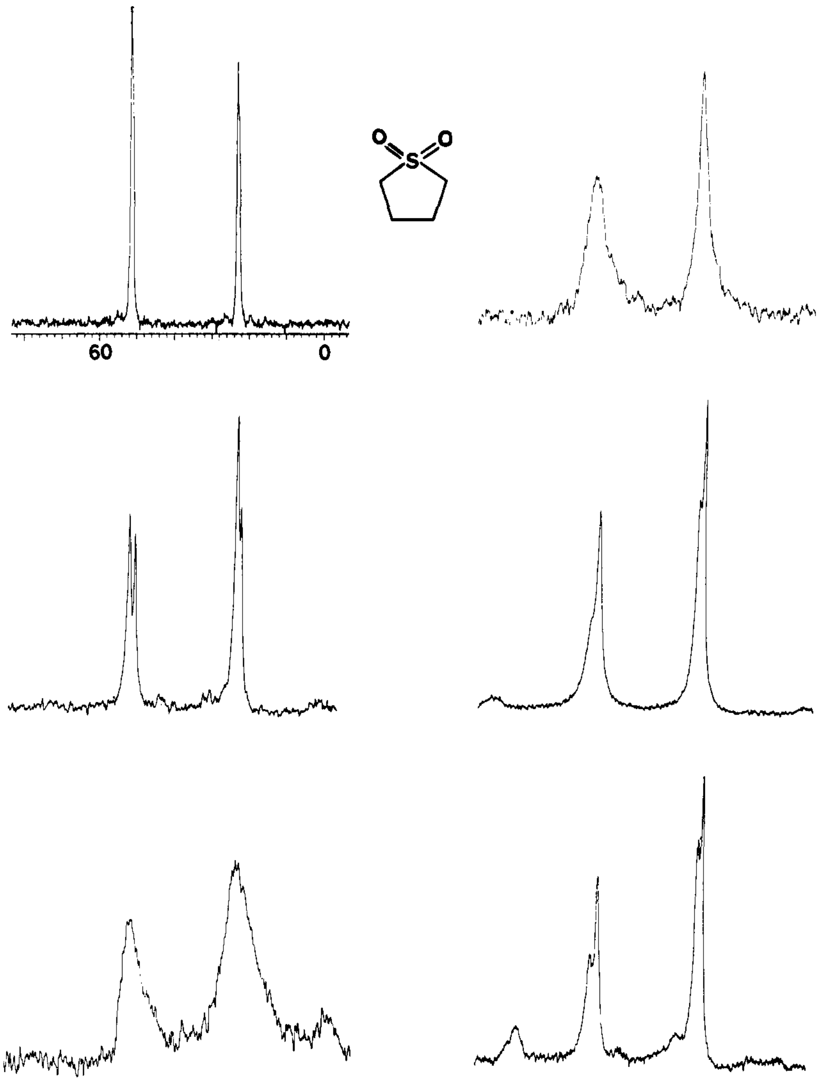

**Figure 9.** Carbon-13 CP/MAS spectra of sulfolane (from top left) at +38, -5, and -40 °C and (from top right) at -55, -70, and -80 °C.

addition, there are several ways that a single form can give rise to multiple resonances for a given type of carbon. There can be more than one independent molecule within the asymmetric unit, dissymetry or disorder within the asymmetric unit, or multiple domains or phases within the solid. The last possibility is unlikely, as spectral behavior was always reproducible and did not evolve in time.

We cannot specify which phenomena contribute to the spectral multiplicities, but we can state unequivocally that there are at least two forms of cyclopentanol in the solid and that these forms are in equilibrium but do not interconvert rapidly on the NMR time scale below -73 °C. A single molecule can never have more than two different C2 or C3 carbons, but the spectrum clearly has up to four of each to -80 °C and up to eight below -100 °C.[12] We can group the explanations into three general categories. (1) Conformational, encompassing the first four explanations: The multiple forms may then be familial, positional, geminal, or rotational. (2) Hydrogen bonded: For example, the symmetry of the spectra to -100 °C could be explained in terms of slowly interconverting monomers (**1**) and dimers (**2**). If the monomer does not have an average plane of symmetry because of slow conformational processes, C2 and C3 would each give two peaks. The dimer also has two different C2 and C3 positions. Trimers and higher oligomers may be present, but by Occam's Razor we need not invoke them. (3) Multiplicities within the asymmetric unit. Further insight into the structure was obtained from the spectra of the *O*-deuterated derivative and of cyclohexanol.

**Cyclopentanol-*OD*.** The presence of deuterium lowers the freezing point and alters the plastic-to-nonplastic transition temperature. There are clear differences between the NMR spectra (compare Figures 1 and 2), but the deuterated derivative still shows spectral multiplicities below -100 °C. This observation eliminates explanations in terms of conformations or the asymmetric unit as the sole cause of the multiplicities, because it is unlikely that H vs D would have a profound effect on the familial, positional, geminal, or rotational properties or the structure of the asymmetric unit. The change from H to D, however, would affect the structure and dynamics of hydrogen-bonded aggregates. Thus the spectrum of the OD derivative requires that hydrogen-bonded aggregates contribute to the spectral multiplicities, although other explanations are not eliminated as being contributory.

**Cyclohexanol.** This six-membered ring is a useful model, because only one family (chair) is possible, pseudorotation is absent, there are no positional forms, and there are only two geminal forms (axial and equatorial). The spectrum of cyclohexanol (Figure 3) passes through a broadening process and reemerges at -80 °C with the same overall appearance as at -40 °C, although the resonances of C3 and C4 have merged. By -100 °C, however, further broadening occurs and the resonance of C2 splits into two. This latter change can be explained in terms of a single form, such as equatorial cyclohexanol with a slowly rotating hydroxy group. It is not necessary to invoke two forms, such as axial and equatorial. A hydrogen-bonded dimer analogous to **2** also by itself could explain the spectrum.

The plastic-to-nonplastic transition for cyclohexanol occurs at

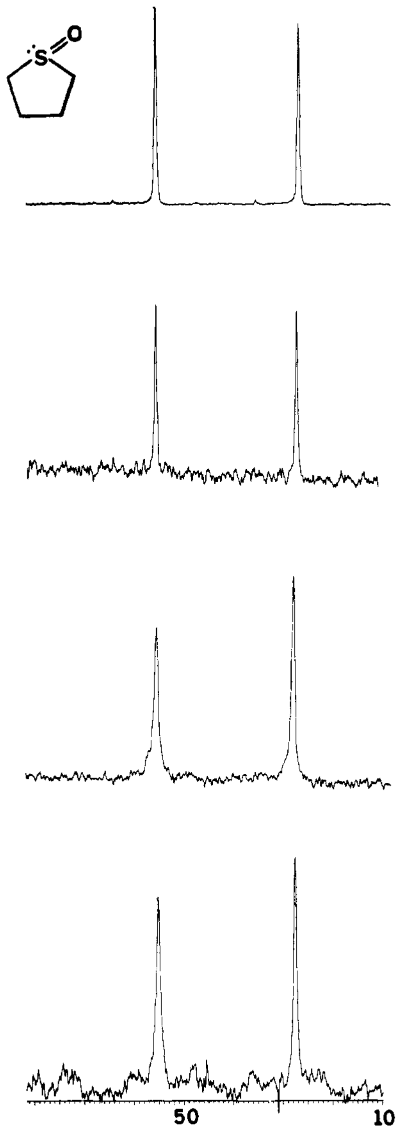

**Figure 10.** Carbon-13 CP/MAS spectra of tetrahydrothiophene 1-oxide (from top) at -10, -50, -75, and -85 °C.

**Table 1.** Free Energies of Activation

| | $T_c$, K | $\Delta G^\ddagger$, kcal mol$^{-1}$ |
|---|---|---|
| cyclopentanol | 210 | 9.8 |
| cyclopentanol-*OD* | 193 | 9.1 |
| cyclohexanol | 188 | 8.9 |
| *trans*-1,2-cyclohexanediol | 313 | 15.2 |
| sulfolane | 288 | 13.9 |

-8 °C, but the substance is very easily supercooled through this transition to a glass transition at -123 °C. There are also several metastable phases that depend on the thermal history of the sample.[16] Examination of longitudinal relaxation times of supercooled cyclohexanol indicated that there are two different types of motion: overall molecular rotation and internal rotation of the cyclohexyl ring about the C–O bond with the COH group fixed in the lattice.[22] On the basis of our spectra, it was not possible to determine if the sample had undergone the plastic-to-nonplastic transition at -8 °C, but we believe that by -100 °C the sample is no longer in the plastic phase.

A dramatic broadening of the spectrum occurs between -20 and -80 °C, without decoalescence at the low-temperature extreme. This phenomenon most likely results from comparability of the frequencies of the incoherent molecular motion of the five-membered rings and of the coherent $^1$H decoupler.[23] When these frequencies are similar, the efficiency of dipolar decoupling is reduced with the result that dipolar line broadening is present. The frequency comparability is absent at higher and lower temperatures, so narrow lines are observed above and below the critical range. Since the broadening is not related to the interconversion of two forms, there is no decoalescence when resharpening occurs at low-temperatures. Rothwell and Waugh found similar *maximum dipolar broadening* for the plastic crystal temperature range for hexamethylbenzene and adamantane, and Twyman and Dobson[24] attributed similar broadening to phenyl rotation. We repeated our experiment with cyclohexanol at a variety of cooling rates but always obtained the same set of spectra at the same temperatures. An alternative mechanism of line broadening has been observed by Riddell and co-workers.[10] When motional frequencies are similar to the frequency of the $^{13}$C spin lock, the spin-lock relaxation time and hence signal intensities are reduced.[10] This latter source of line broadening is not observed when single pulses rather than the CP method are used. Maximum dipolar broadening does not involve loss of signal intensity. We have not endeavored to distinguish the two phenomena, and both may be present. Observation of line broadening as in Figure 3 is clear evidence in either case for molecular motion in the solid. For plastic crystals, the molecules are undergoing overall motion or possibly motion along a preferred axis.

**Cyclopentanone.** The spectra of cyclopentanone contrast with all those of the above alcohols (Figure 4). This molecule has no plastic phase.[19] It freezes directly from the liquid to a nonplastic phase, in which cyclopentanone is presumably nonrotating. Although the freezing point of cyclopentanone is -51 °C, we observed some supercooling, followed by freezing at about -80 °C, as indicated by the appearance of spinning sidebands for the carbonyl resonance and the spectral improvement with cross polarization. Simultaneous with freezing was decoalescence of the C1 and C2 peaks into doublets of approximately equal intensity. Calculations have favored a $C_2$ (half-chair) conformation with restricted pseudorotation.[7] The spectral doubling requires that there are two magnetically nonequivalent positions in the solid. To date, no X-ray experiment has been able to examine cyclopentanone. It is possible that a single conformation exists in two crystallographically distinct positions in the asymmetric unit. Alternatively, two different conformations may be present.

**Cyclohexanone.** The observation of spinning sidebands for C1 indicates that cyclohexanone has frozen by -55 °C (Figure 5). There is a slight broadening of the resonances at this temperature, probably due to dipolar or $T_{1\rho}$ effects. When the peaks sharpen again, they closely resemble the liquid spectrum. The lack of spectral multiplicity at low temperatures indicates that only one form is present in the solid, as expected for the single, chair conformation of cyclohexanone.

**1-Methylcyclopentanol.** This molecule is not globular and probably does not have a plastic phase. After freezing, there are no spectral changes, although the resonance of C2 is broader than the other peaks and shows a doubling. Thus there may be two positions or two forms of this molecule in the solid.

***trans*-1,2-Cyclopentanediol.** Below its freezing point, this molecule undergoes severe, reversible peak broadening that does not lead to spectral decoalescence at lower temperatures, indicative of maximum dipolar broadening (Figure 7). The broadening occurs at higher temperatures than for cyclohexanol, so that motion of the diol is slower, as might be expected for a more extensive hydrogen bonding network. There is no evidence for multiple forms at low-temperatures.

***trans*-1,2-Cyclohexanediol.** Below the freezing point both methylene resonances split into two peaks of approximately equal

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intensity (Figure 8). If this spectral multiplicity arose from the presence of diaxial and diequatorial conformations, the C1 peak should split in the usual fashion into a doublet with a separation of some 4 ppm. The substituted carbon is almost always the most sensitive to conformational effects in six-membered rings. Because C1 remains a singlet, we believe that the splitting is not due to geminal nonequivalence. Intramolecular hydrogen bonding in the diequatorial form should lead to two different C1, C2, and C3 positions. If the C1 splitting for some reason is small, this is the most economical explanation of the spectrum. Alternatively, there may be two different aggregational forms, e.g., monomer and dimer, or simply dissymmetry within the asymmetric unit. The absence of maximum dipolar broadening suggests that overall molecular rotation is slow. The diol barrier is higher than that for the simple alcohols (Table 1).

**Sulfolane.** This molecule freezes near room temperature to a plastic form and undergoes conversion to the nonplastic form at +15 °C. This latter phase transition is accompanied in the spectrum by decoalescence into two peaks of unequal intensity (Figure 9). The inequality is significant because it means that the spectrum cannot be interpreted in terms of two crystallographically different positions in the asymmetric unit. Therefore, it is likely that sulfolane exists in two conformationally distinct forms in the nonplastic phase. As there are no hydroxyl groups, and the identical geminal oxygens are incapable of rotation, the only possibilities are two conformational families or two positional isomers.

Between 0 and –70 °C, maximum dipolar broadening is observed, so that there must still be motion within the crystal below the plastic-to-nonplastic phase transition. Moreover, cross polarization does not improve the spectrum until –70 °C. These observations are consistent with the proposed additional phase transition at –63 °C that could involve further diminution of molecular motions.[17] When the sharp peaks reemerge at –70 °C, there are still only two peaks per resonance, but the relative intensities have changed. It is possible but unlikely that the peaks have switched positions. It is more likely that the two conformational forms are in equilibrium on the laboratory time scale, and at lower temperatures the relative amounts of the two forms have changed.

**Tetrahydrothiophene 1-Oxide.** This molecule freezes directly to the nonplastic state. The lack of motion within this state is confirmed by the absence of maximum dipolar broadening (Figure 10), although there appears to be a slight sharpening at –95 °C. The absence of splitting indicates that the molecule exists in a single form in the solid.

## Summary

Of the ten molecules examined in this study, hardly any two have the same spectral behavior in the solid (Figures 1–10). Nonetheless, all the spectral changes that occur in the solid phase may be explained in terms of three phenomena.

**Plastic Phases.** Globular molecules can freeze into a plastic phase in which rotation takes place at the lattice positions within the solid. As a result, the solid-state spectrum takes on the overall symmetry that is normally characteristic of the liquid phase, and prominent spinning sidebands are not observed for nuclei such as carbonyl carbons with highly anisotropic shielding tensors. This phenomenon is observed between the freezing point and the plastic-to-nonplastic transition for cyclopentanol, cyclohexanol, cyclohexanone, sulfolane, and possibly *trans*-1,2-cyclopentanediol. For these molecules, decoalescence can be observed at the plastic-to-nonplastic transition, leading to a more complex spectrum characteristic of the structure and symmetry of the nonrotating molecules in the solid. Cyclopentanone and probably tetrahydrothiophene 1-oxide freeze directly into a nonplastic phase.

**Maximum Dipolar Broadening.** When rapid overall molecular motion in a plastic phase, segmental motion within a molecule, or residual but restricted molecular motion in a nonplastic phase is comparable in frequency to that of the $^1$H decoupler, significant peak broadening can occur.[23] This phenomenon has a profound effect on the spectra of cyclohexanol and *trans*-1,2-cyclopentanediol, the effect is significant for sulfolane, and there is a modest effect for cyclohexanone. Loss of intensity also may occur when the motional frequency is similar to the $^{13}$C spin-lock frequency and $T_{1\rho}$ is reduced appreciably.[10] Because these phenomena are due to molecular motion without chemical exchange, decoalescence does not occur at the low-temperature extreme.

**Site Exchange.** Spectral multiplicity can arise when exchange becomes slow on the NMR time scale either between nonequivalent forms or between nonequivalent sites within a single form. The slow-exchange spectra of cyclopentanol and of sulfolane clearly indicate that there are respectively several and two unequally populated forms in the solid. Certain resonances in the spectra of cyclohexanol, cyclopentanone, 1-methylcyclopentanol, and *trans*-1,2-cyclohexanediol split into two peaks of equal intensity. Such observations may arise either from the presence of two equally populated species (conformers, positional isomers, crystallographic sites) or from a single form with two sites that are capable of exchange to a single averaged site upon the onset of molecular rotation. For the case of cyclopentanone the latter explanation may be excluded, because the carbonyl carbon splits into two, which is only possible when two forms are present.

Because of rapid internal and overall motions of five-membered rings, it is clear that solution spectra have hidden a vast array of structural properties. Even very common rings, such as those studied herein, can have multiple forms in the solid that heretofore were either unsuspected or undetected.

## Experimental Section

Samples were commercially available, with the exception of cyclopentanol-*OD*, which was prepared by treatment of cyclopentanol with Na and $D_2O$ in the absence of solvent (>95% deuteration by MS), and *trans*-1,2-cyclopentanediol, which was prepared by ring opening of cyclopentene oxide.[25]

Solid-state spectra were recorded on a Varian VXR 300 spectrometer equipped with a Doty 7-mm probe with variable-temperature accessory. The liquid was loaded into a sapphire rotor with either macor O-ring or Kel-F screw caps. The rotor was inserted into the probe and spun slowly (<600 Hz) until the sample had frozen. The spinning rate then was increased to the maximum possible for the temperature, usually between 1500 and 4000 Hz. The spinning rate generally increased at lower temperatures. The nitrogen used for sample spinning was precooled by circulation through liquid nitrogen, and the temperature was regulated by heating this gas. The temperature was measured in the probe before the gas supply reached the sample. The actual temperature was determined with samarium acetate tetrahydrate[26] under identical conditions to those for the other samples and was found to be 15–20 °C warmer than the console reading below ambient. The combination of frictional heating from spinning and the fact that the console reading is carried out on gas before it reaches the sample cause this temperature discrepancy.[27] Cross polarization was used for all solid samples when efficacious. All spectra were recorded both on lowering and on raising the temperature to ensure reproducibility. Chemical shifts were referenced to hexamethylbenzene and then scaled to TMS.

Phase transitions were identified with a Perkin-Elmer DSC-2 or DSC-7 differential scanning calorimeter with hermetically sealed sample pans and either liquid $N_2$ or dry ice/acetone as a cooling bath. Temperature scales were calibrated from known phase transitions within the appropriate temperature range. All scans were recorded upon both heating and cooling to determine hysteresis effects. Solid samples were melted first to remove any thermal history.

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