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Molecular Motions in Four Medium-size Cyclic Ketones

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Molecular Motions in Four Medium-size Cyclic Ketones

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Abstract—The proton magnetic resonance of cyclohexanone, cycloheptanone, cyclooctanone and cyclononanone has been investigated. Near the solid–solid transitions, both the linewidth and the second moment decrease to values indicating the onset of quasi-isotropic reorientation. In the case of cyclohexanone and cycloheptanone, this is accompanied immediately by translational diffusion of the molecules. For cyclooctanone and cyclononanone, diffusion begins to be observable in a temperature range intermediate between the transition and melting points.

1. Introduction

Some molecular solids, which possess an abnormally low fusion entropy and a high melting point, may exhibit a crystalline phase with a relatively high symmetry, known as a " plastic crystal ",⁽¹⁾ just below the melting point. They undergo, at lower temperatures, one or more solid phase transformations to a less symmetrical crystalline system.

Nuclear magnetic resonance (NMR) constitutes a valuable tool for studying the molecular processes occurring in the solid state: the temperature dependence of linewidth and second moment of the NMR spectrum suffices to establish the existence and the nature of the motions and gives an indication on the reorientational dynamics. Indeed molecular motions whose frequency is greater than 10^4 Hz, reduce the average magnetic dipolar interactions between the nuclei and bring on a spectral narrowing.

We have done such a study on four medium size cycloalkanones of nearly spheroidal shape: cyclohexanone (CHX), cycloheptanone (CHP), cyclooctanone (CO) and cyclononanone (CN). Unfortunately, a precise analysis of their molecular behaviour was greatly hindered by the lack of accurate thermodynamical and structural data.

Data about phase transitions are not available directly from calorimetric measurements. The physical methods which indicate the existence of different crystalline modifications are DTA for CO and CN,(2) determinations of dielectric permittivity for CHX(3,4,5) and CHP,(5) IR spectroscopy for the four compounds.(6) The results are summarized in Table 1.

TABLE 1. Thermodynamical Properties of Cycloalkanones

	CHX	CHP	CO	CN
T_F (K)	241	252	315	301
ΔS_F (u.e.)	—	—	2(2)	1.5(2)
TR_{I} (K)	221 ± 3	221.5 ± 2.5	231 ± 2	191 ± 3
$\Delta S_{TR_{\mathrm{I}}}$ (u.e.)	—	—	17(2)	—
TR_{II} (K)	NO	NO	186 ± 2	NO
$\Delta S_{TR_{\mathrm{II}}}$ (u.e.)			4(2)	

We remark that only CO possesses two solid–solid phase transitions, which could be observed only by differential scanning calorimetry(2); the earlier study using IR spectroscopy(6) showed none.

The crystallographical structures known are those of the phase I of CHX,(7) the phases I and III of CO(2)† and the phase I of CN.(2) Results are reported in Table 2.

TABLE 2. Crystallographical Data of Crystalline Cycloalkanones

	CHX(7)	CO(2)		CN(2)
Phase	I	I	III	I
T (K)	218	298	168	288
Crystal system	Cubic	Cubic	Monoclinic	Cubic
Lattice parameter (Å)	8.61	11.97 ± 0.02	$a = 11.37$ $b = 11.61$ $c = 11.69$ $\beta = 95.10°$	12.33 ± 0.05
Space group	—	Pm3n	—	Pm3n
Molecules/unit cell	4	8	8	8

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† Phases are numbered from I to III in order of decreasing temperatures.

It is interesting to note that for the two last compounds the crystal data are nearly identical with those observed for cyclooctane,⁽⁸⁾ i.e. a cubic system with a *Pm*3*n* space group. The molecular arrangement suggested by Sands and Day has 6 molecules in positions (c) and two molecules in positions (a). Alternative arrangements using 8 equivalent positions on sites (e), or the combination 6(b) plus 2(a) were excluded because they were not consistent with the X-rays data.

However the lack of knowledge of molecular structures leads to a difficulty. Is there one or more conformations stable in the solid state, and what are they?

Dale(9) studying the variation in enthalpies of formation, stability and transformation points tries to explain the conformations of the cycloalkanes and cycloalkanones. He first concludes that the cycloalkanones should behave conformationally like the cycloalkanes and that there is a group of high " apparent " melting point cyclanes from C_6 to C_{11}, just around cyclooctane for which the proposed conformation has a practically spheroidal shape. From the IR studies,(10,11) it has been found that the final selection of conformations for the crystal lattice must take place just below the transition. So in the lower solid phase, there is one favorable conformation which must obey, moreover, two principles: there is no strain-free-conformation and, because of close-packing tendency, the most compact conformation is favored over that with a large hole inside. So with the supplementary informations given by the machine-computation(12) of conformation as a function of various geometric parameters, the conformational analysis(13) and the calculation of strain energy minimization,(14) we have selected the following conformations for the interpretation given in Sec. 3:

—for the cyclohexanone, a " chair " conformation.

—for the cycloheptanone, a so-called " chair " conformation with the $>C=0$ substituent in position 3, the steric repulsion between the axial hydrogens attached on the carbons 3 and 6 being thus suppressed.

—for the cyclooctanone, a " crown " conformation with the " O-outside ".

—for the cyclononanone, a more complex form.

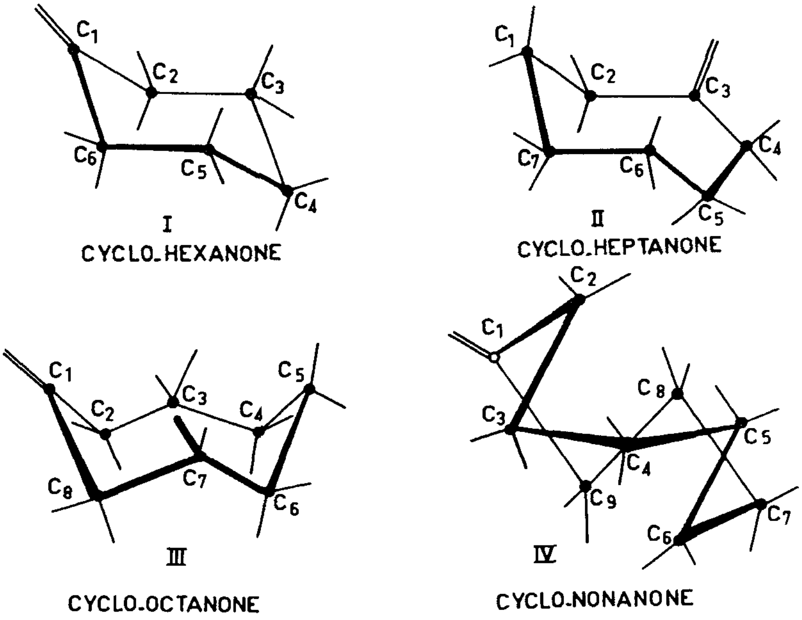

Figure 1. Dreiding's stereo models of cycloalkanones.

These conformations are represented on Fig. I.

2. Experimental

2.1. Method of Measurements

The magnetic resonance absorption measurements were made with a standard Trüb–Tauber apparatus. The steady magnetic field was supplied by a permanent magnet producing about 5850 G, so that the proton resonance occurred at a frequency of 25 MHz. Lock-in detection at 30 Hz gave the first derivative of the absorption line shape. The sample containers were inserted in an especially designed cryostat cooled with a controlled flow of nitrogen gas passing through a spiral tubing immersed in liquid nitrogen. The absolute accuracy of the temperature measurements was about 1 K.

The samples used for these investigations were obtained from Merck Laboratories, Shuchardt Laboratories and Columbia Organic Chemical Co. In each case, the purity was better than 99.9%. The samples were carefully degased and then vacuum-distilled from the original containers into suitable glass tubes which were then sealed off.

All measurements were made with increasing temperatures. Several annealings near the thermodynamical transitions were carried out. To ensure both thermic and thermodynamical equilibrium, we waited for at least half an hour before recording each spectrum.

2.2. Results

The variations with temperature of the linewidth $\overline{\Delta H}$ and the second moment $\overline{\Delta H^2}$ of the NMR spectra are shown in Figs. 2, 3, 4 and 5 for the four cycloalkanones respectively.

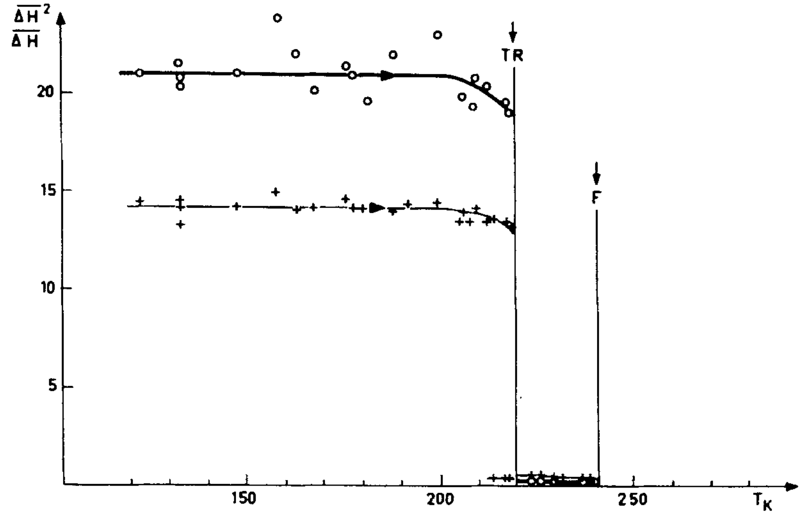

Figure 2. Temperature dependence of the width (+ + +) and the second moment (° ° ° °) of the NMR spectra of cyclohexanone.

Below the transition temperatures, $\overline{\Delta H}$ and $\overline{\Delta H^2}$ achieve constant values which are reported in Table 3. In these regions, the results are subject to a rather large error: too fast a saturation of the absorption signal, probably due to a long spin–lattice relaxation time T_1 leads to an unfavourable signal-to-noise ratio. This fact seems

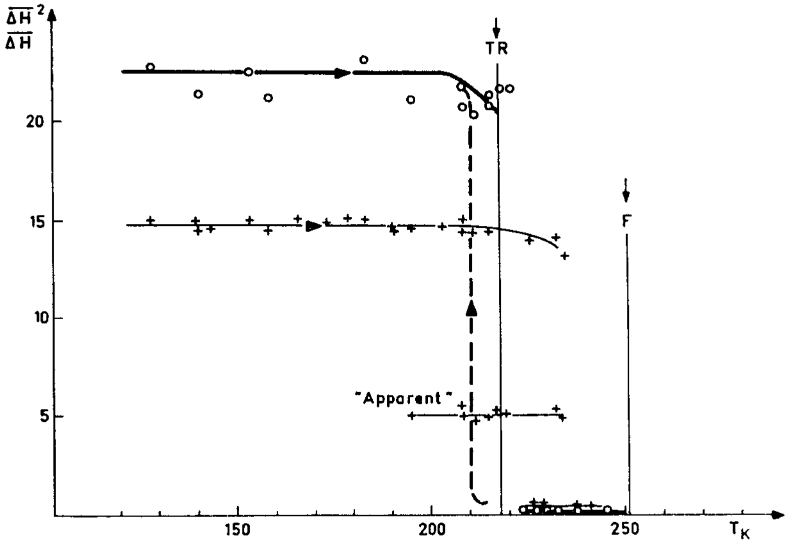

Figure 3. Temperature dependence of the width (+ + +) and the second moment (°°°°) of the NMR spectra of cycloheptanone. Continuous lines represent heating data; dotted lines, cooling data.

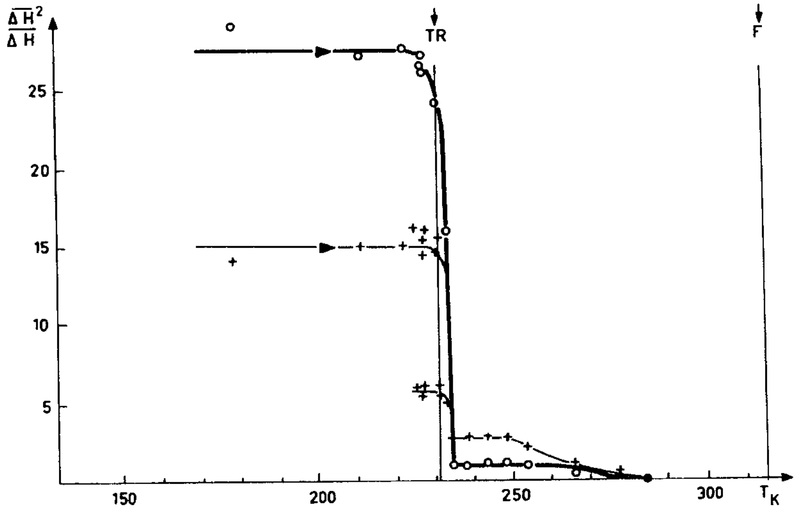

Figure 4. Temperature dependence of the width (+ + +) and the second moment (°°°°) of the NMR spectra of cyclooctanone.

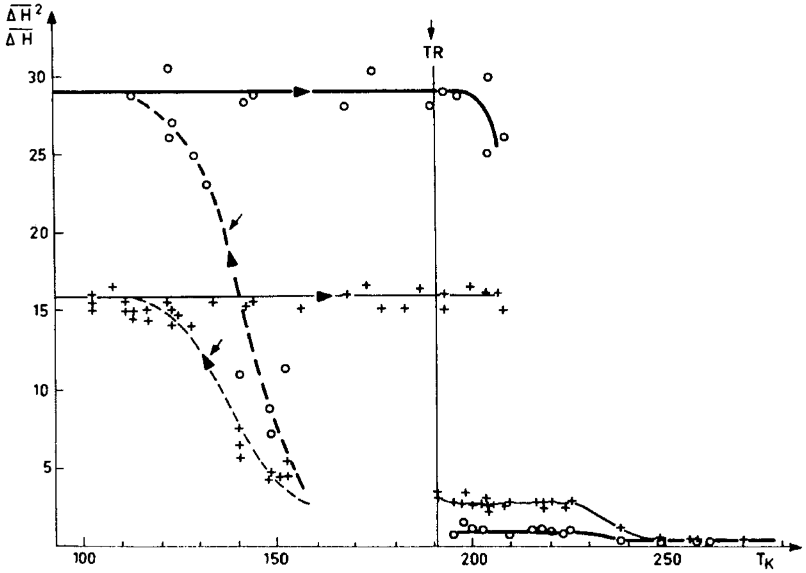

Figure 5. Temperature dependence of the width (+ + +) and the second moment (° ° ° °) of the NMR spectra of cyclononanone. Continuous lines represent heating data; dotted lines, cooling data.

especially important in the case of the CN where the resonance line remains assymetric even after having decreased the relaxation time by introducing free radicals in the lattice through γ-irradiation.

When the transformation point is approached, the line begins to narrow and shows in all cases evidence of fine structure. Attempts to resolve the narrow component were successful only for CHP, in which case the real width of the narrow component (after reducing the modulation amplitude) was found to be 1 G.

In the case of CHX and CO, at the transition temperatures themselves, the lines show a rather abrupt decrease. For CHP and CN, this change occurs about 15 K above the transition. Then, a new plateau is reached (the corresponding values are reported in Table 3) which is wider in the case of CN than in that of CO and unobservable for the CHP and CN. The line narrows further until the apparent width is wholly governed by the magnetic field inhomogeneity.†

Supercooling effects down to 20 K below the solid state transition have been observed in the case of CHP and CN.

3. Discussion

3.1. Rigid Lattice Value

The calculation of the theoretical second moment of a rigid lattice can be divided into that of the intra and that of the intermolecular contributions:

—The intramolecular contribution may be calculated by applying the Van Vleck(15) formula for polycrystalline material:

$$\overline{\Delta H^2_{\text{intra}}} = 358.1\, N^{-1} \sum_{j,k} r_{jk}^{-6} \tag{1}$$

where N is the number of nuclei considered and r_{jk} the internuclear distance in Å between the nuclei j and k, measured on the Dreiding's stereo-models reproducing the molecular structures described on *Part I* of this paper.

—The calculation of the intermolecular contribution requires the complete knowledge of the lattice structure of the low temperature form. As these data are not available, we made an estimation by comparison with other similar compounds such as adamantane,(16) cyclohexane,(17) cyclooctane,(18) cyclodecane(19) and cycloheptatriene.(20) The theoretical values thus obtained are in good agreement with the experimental ones as shown in Table 3. We conclude that, at low temperatures, the lattice is effectively rigid, i.e. the lattice is orientationally ordered. (It could also in principle be disordered with a characteristic time for the rearrangement of the disorder smaller than 10^{-4} sec, but such an hypothesis is unlikely because of the absence of transitions at still lower temperatures.)

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† Our results concerning the cyclooctanone are different from those of Rudman and Post.(2) These authors observe at temperatures below 183 K a splitting of the line shape which is attributed to the methylene group, the value of the second moment of the broad line being 43 G^2. Above 225 K, the line decreases progressively to a very low value.

TABLE 3 Theoretical and Experimental NMR Results
For explanation of hypothesis I and II, see text

		Theoretical			Experimental	
		$\overline{\Delta H}^2_{\text{Intra}}(G^2)$	$\overline{\Delta H}^2_{\text{Inter}}(G^2)$	$\overline{\Delta H}^2_{\text{total}}(G^2)$	$\overline{\Delta H}(G)$	$\overline{\Delta H}^2(G)^2$
C.H.X.	Rigid lattice $T < 200$ K	14.5 ± 0.5	6 ± 1.5	20.5 ± 2	14.2 ± 0.5	21 ± 2
	Isotropic reorientation	0	1.02	1.02	< (no plateau)	
C.H.P.	Rigid lattice $T < 200$ K	18 ± 1	6 ± 1.5	24 ± 2.5	14.8 ± 0.5	23 ± 2.5
	Isotropic reorientation	0	?	1 (supposed)	< (no plateau)	
C.O.	Rigid lattice $T < 220$ K	20 ± 1.5	6.5 ± 1.5	26.5 ± 3	15 ± 1	27.5 ± 2
	Isotropic reorientation	0	I 0.808 II 0.917	0.808 0.917	2.75 ± 0.1	1.10 ± 0.1
C.N.	Rigid lattice $T <$ TR	23.5 ± 3	6 ± 1.5	29.5 ± 4.5	15.5 ± 1	29 ± 3.5
	Isotropic reorientation	0	I 0.773 II 0.877	0.773 0.877	2.7 ± 0.1	0.90 ± 0.1

3.2. SPECTRAL NARROWING

Three reasons may be brought forward to explain the slight decrease of the linewidth and of the second moment as the transition is approached: the lattice dilatation, the effect of the ring puckering or the presence of a narrow line which is attributed to the reorientation of some molecules near the lattice imperfections.

For CHX and CO, we observe a discontinuity of the linewidth and the second moment of the spectral line at the transition, indicating the appearance of the reorientational movement. In the cases of CHP and CN, this process seems to be more sluggish. We note, indeed, a delay in the transition: movements could exist, but if they have a frequency lower than 10^5 Hz, they do not affect the resonance line shape.

3.3. THE HIGH TEMPERATURE PHASE

Making the assumption of a quasi-isotropic reorientational motion, we determined the values of the second moment of the absorption line in the three cases where the lattice parameters are known. The intramolecular is then zero, while the intermolecular contribution is calculated by supposing(17,22) that all molecular protons are concentrated at the molecular centers. One has thus for protons:

$$\overline{\Delta H^2} = 358.1\, N_0\, a^{-6}\, S$$

where $\overline{\Delta H^2}$ is the second moment in G^2, a is the cubic cell translation in Å, N_0 is the number of protons per molecule and

$$S \equiv \sum^{\infty} \left(\frac{r_j}{a}\right)^{-6}$$

is a lattice sum which depends on the number and positions of the molecules in the cubic cell.

For CHX, the molecules are on the sites of a fcc lattice and we used the fcc lattice sum computed by Jones and Ingham's(21):

$$S = 115.631$$

For CO and CN, we have computed the required simple cubic sum with different molecular arrangements. For the arrangement 6(c) + 2(a), called I in Table 3, we find $S = 473.76$. For the arrangement

8(e)†, called II, we find $S = 537.71$.‡ The results are listed in Table 3.

In the case of CO and CN, the best agreement between experimental and theoretical values is given by the hypothesis of the molecular arrangement II which contains 8 equivalent positions. However the assumption that the molecular centers are fixed on the lattice sites is not necessarily valid. Indeed the distances between the molecular centers in the lattice are less than the Van der Waals diameters of the rotating crown. The crowding may be alleviated by a correlated displacement of the molecules. So the quasi-isotropic reorientation cannot be free and is a cooperative phenomenum.

For CHX and CHP, the experimental second moment values is much less than the calculated one; we must therefore suppose a further molecular motion, probably a molecular diffusion process, typical of plastic crystals. Such a motion, besides, is certainly responsible for the progressive decrease of the linewidth observed at temperatures higher than those of the plateaux of CO and CN. The most likely mechanism for this diffusion is the migration of point defects such as vacancies.(23,24)

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† The two molecular arrangements 8(e) and 6(b) plus 2(a) are different but correspond to the same lattice of points, which is a simple cubic one with translation $a/2$.

‡ These lattice sums have been computed including 1728 and 1000 molecules respectively for the arrangements I and II plus a continuum representing the molecules beyond.

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