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Order-disorder transitions in adamantane derivatives: vibrational spectroscopic and ^{13}C NMR studies of 1-chloroadamantane

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YINING HUANG, RALPH M. PAROLI, D.F.R. GILSON, and I.S. BUTLER. *Can. J. Chem.* **71**, 1890 (1993).

The order-disorder behaviour of 1-chloroadamantane ($1\text{-C}_{10}\text{H}_{15}\text{Cl}$) has been investigated by differential scanning calorimetry, and variable-temperature vibrational and ^{13}C NMR spectroscopy. The factor group splittings in the vibrational spectra are in accord with the known crystal structures of the two phases. The ^{13}C spin-lattice relaxation times and dipolar dephasing measurements have been analysed to give the barriers to rotation in both phases and to determine the nature of the rotations in each phase. In the ordered phase, the motion is limited to rotation about the molecular axis. In the disordered phase, additional motions occur about axes through the tertiary carbon atoms.

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Faisant appel à la calorimétrie à balayage différentielle, à la RMN du ^{13}C et à la spectroscopie vibrationnelle à température variable, on a étudié le comportement ordre-désordre du 1-chloroadamantane ($1\text{-C}_{10}\text{H}_{15}\text{Cl}$). Les dédoublements des facteurs de groupe des spectres de vibration sont en accord avec les structures cristallines connues des deux phases. On a analysé les temps de relaxation spin-réseau du ^{13}C et les mesures de déphasage dipolaire pour obtenir les barrières à la rotation dans les deux phases et pour déterminer la nature des rotations dans chaque phase. Dans la phase ordonnée, la mouvement se limite à une rotation autour de l'axe moléculaire. Dans la phase désordonnée, des mouvements additionnels se produisent autour des axes des atomes de carbone tertiaires.

[Traduit par la rédaction]

Introduction

Adamantane and many of its derivatives possess orientationally disordered structures (1–3) in which the high-temperature phases are usually characterized by extensive molecular motions about one or more axes and, in some cases, translational diffusion (4–11). Interpretations of the mechanisms of the transition to the ordered phase are hindered by the lack of information on the crystal structure of the low-temperature ordered phase and the molecular dynamics associated with the transition. The 1-haloadamantanes, although they have the same molecular symmetry, exhibit marked differences in their phase transition behaviour (2, 3). 1-Fluoroadamantane displays one solid-solid phase transition, but this phase change is not of the order-disorder type (3–5) and both phases are orientationally disordered. On the other hand, 1-chloro- and 1-bromoadamantane have disordered high-temperature phases and undergo one and two phase transformations, respectively, with the lowest temperature phases being ordered. The 1-iodo compound also has a single phase transition but overall molecular tumbling in the high-temperature phase does not occur and the molecules only undergo a 12-fold uniaxial rotation (6).

1-Chloroadamantane, where the melting and transition temperatures are 442.5 and 244.2 K with transition entropies of 11.01 and 24.61 J K⁻¹ mol⁻¹, respectively (2), is one of few compounds for which the crystal structures of both the ordered and disordered phases have been reported (7, 8). The low entropy of fusion indicates that the high-temperature phase is disordered, and, in common with most singly substituted adamantane derivatives, the structure is face-centred cubic, space group $Fm\bar{3}m$, with four molecules per unit cell. The ordered phase is monoclinic, space group $P2_1/c$, also with four molecules per unit cell.

Although 1-chloroadamantane has been investigated by several different experimental methods, the molecular dynamics remain unclear, especially for the disordered phase

(9–11). On the basis of proton NMR studies, Virlet et al. (6) concluded that the motion in phase I of 1-bromoadamantane is a fast endospherical reorientation. Using the same technique, Ursu et al. (9, 11) suggested that the motion in phase I for both 1-chloro- and 1-bromoadamantane is a combination of a rotation about the molecular C_3 axis and a jump reorientation of this axis in the lattice, but did not specify about which crystallographic axes this reorientation of the C_3 axis is taking place. In the low-temperature phase, only one barrier was indicated by proton T_1 measurements and a C_3 uniaxial rotation was assumed to be responsible for the relaxation (9).

The results of an incoherent quasi-elastic neutron scattering study have suggested that there are two types of motion occurring in the high-temperature phase of 1-chloroadamantane: tumbling of the molecular C_3 axis among six fourfold crystallographic axes along the [100] directions, and a uniaxial rotation about the molecular threefold axis (10). The barrier to molecular tumbling is about twice that of uniaxial rotation. Incoherent neutron scattering studies have been widely used to provide models of the molecular motions in plastic crystals. Since the timescale of neutron scattering is fast, this technique is particularly useful for characterizing motions on the timescale of 10^{-11} to 10^{-13} s. However, this method offers little information about the slower motions in the disordered phases. NMR spectroscopic methods, however, are more sensitive to the presence of slow motions and can be used to detect such motions in both disordered and ordered phases, determine the barriers to motions, and identify the nature of the reorientations.

The factor group method (12), by which the splittings of vibrational peaks can be correlated with the changes in symmetry that occur at the phase transition, provides an indirect method of obtaining structural information. In the present work, we have examined the FT-IR and Raman spectra of the two different phases of 1-chloroadamantane and measured ^{13}C spin-lattice relaxation times and dipolar dephasing times. The dipolar dephasing technique has been

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widely used to obtain chemical structural information and to assign the resonance signals. Although it is well known (13, 14) that molecular motion has a great impact on the dephasing of carbon signals, especially for methylene and methine carbons, this method has not been widely used in the study of molecular motions. However, the technique can be readily used to identify the motions existing in orientationally disordered crystals, such as 1-substituted adamantane derivatives (15).

Experimental

1-Chloroadamantane ($1\text{-C}_{10}\text{H}_{15}\text{Cl}$, Alfa products, 98%) was purified by repeated slow vacuum sublimation (21°C , 10^{-3} Torr; 1 Torr = 133.3 Pa). The purified material was analyzed by gas chromatography and was greater than 99.5% pure.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-7 calorimeter, calibrated for both temperature and enthalpy scales using the phase and melting transitions of cyclohexane (Aldrich Chemical Co., "Gold" grade), at a scanning rate of 2.5 K min^{-1} .

The IR spectra (1 cm^{-1} resolution) were recorded on an Analect AQS-18 FT-IR spectrometer equipped with a DTGS detector. The spectra were obtained using KBr pellets, which were allowed to relax for at least 1 month prior to use. The Raman spectra ($1\text{--}2\text{ cm}^{-1}$ resolution) were acquired on a Instruments S.A. spectrometer with a Jobin Ramanor U-1000 double monochromator using the 514.5-nm line of a Spectra Physics model 164 argon-ion laser ($\sim 250\text{ mW}$ power at the sample) as the excitation source. The samples were sealed in glass capillary tubes and mounted on the cold finger of a cryostat by using indium foil as the conducting junction. The temperature was controlled, for both the IR and Raman studies, by a Cryodyne Cryocooler model 21 cryostat (Cryogenics Technology Inc.) and was measured with a silicon diode temperature sensor attached to a Cryophysics model 4052 controller.

The ^{13}C spin-lattice relaxation and dipolar dephasing time measurements were performed on a Chemagnetics M100 spectrometer operating at 25.2 MHz . The samples were packed in a bullet-type zirconia rotor (9.5 mm diameter). The sample temperature was regulated to within $\pm 2\text{ K}$ by a Chemagnetics RKC REX-C1000 temperature controller. The ^{13}C spin-lattice relaxation times were measured by the standard inversion-recovery pulse sequence, using seven or more τ values and a delay of at least 5 times T_1 . The 90° pulse widths were between 5 and $6\text{ }\mu\text{s}$. The number of transients required to obtain good signal-to-noise ratios were 32 and 128 for the disordered and ordered phases, respectively. A nonlinear, three-parameter-fit program was used to calculate the T_1 values. The spinning speed of the sample was between 3 and 4 kHz .

The pulse sequence used for the dipolar dephasing experiment was that proposed by Bodenhausen et al. (16) and described by Alemany et al. (14). The contact time for cross polarization was 4 ms for phase II of 1-chloroadamantane but, due to the extensive motion occurring in the high-temperature phase, the carbon spins were difficult to polarize and a 20 ms contact time was necessary.

Results and discussion

The DSC results were obtained for both cooling and heating directions and the transition was observed at 240 and 245 K , with enthalpy and entropy of transition of 5.35 kJ mol^{-1} and $22.0\text{ J K}^{-1}\text{ mol}^{-1}$, respectively. The results are in reasonable agreement with those previously reported (2) except for the small hysteresis in transition temperature. The latter is consistent with the relatively low entropy of transition (17).

Typical vibrational spectra are shown in Figs. 1 and 2. In the infrared spectrum, the broad C—H stretching region displayed considerable splitting when the sample was cooled

FIG. 1. Infrared spectra of phases I and II of 1-chloroadamantane.

from phase I to the ordered phase II. In the remaining regions of the spectrum, nearly all the peaks split into doublets. The notable exceptions were those at 1343 and 1350 cm^{-1} , the CH_2 wag and CCH deformation, respectively, which collapse to a single peak in phase II. The relative intensities of some of the peaks also change at the transition, with the CCC bending and CC stretching (1036 cm^{-1}), CH_2 wagging and CCH deformation (1459 , 1346 cm^{-1}), and C—Cl stretch (828 cm^{-1}) modes showing the most pronounced effects. In the Raman spectra, most of the peaks exhibited the same splitting into two components and the most obvious changes in intensity occurred for the C—C—Cl bend at 215 cm^{-1} , and the C—C—C bend and C—C stretch at 1104 cm^{-1} .

The vibrational representation for the free 1-chloroadamantane molecule transforms as $\Gamma_{\text{vib}} = 16a_1 + 8a_2 + 24e$, where the a_1 and e modes are both IR and Raman active and the a_2 modes are inactive in both the IR and Raman spectra. Thus, there should be a total of 40 IR/Raman active modes, and a total of 29 Raman and 26 IR bands were observed, Table 1. Coincidence of the fundamentals in the infrared and Raman spectra of phase II confirms that the unit cell is not centrosymmetric. Moreover, since the space group of the ordered phase is $P2_1/c$, the $\text{C}_{10}\text{H}_{15}\text{Cl}$ molecule, with molecular symmetry C_{3v} , can only occupy sites with C_1 symmetry in the C_{2h} factor group and all the vibrational modes should split into four components, with the a_g and b_g modes being active in the Raman and the a_u and b_u modes being active in the infrared spectra. The correlation diagram is given in Fig. 3. Since no peak in either spectrum was split into more than a doublet, the observed splittings are in agreement with the factor group predictions.

The spin-lattice relaxation times of the three different protonated carbons, C_β , C_δ , and C_γ , were measured with respect to temperature in both the disordered and ordered phases. Figure 4 shows the temperature dependences of the T_1 values in each phase. In phase I, the T_1 values for all three carbons decreased with decreasing temperature and started approaching a minimum just before the transition tempera-

TABLE 1. Vibrational frequencies (cm^{-1}) for 1-chloroadamantane

Phase I (190 K)		Phase II (300 K)		Assignments
Raman	IR	Raman	IR	
2960s				a_1 CH str.
2954s		2954s		
2940s,sh	2947sh 2939s		2934vs	
2927vs	2928vs	2927vs		a_1, e
2920vs	2920sh 2915vs	2920sh		
2910sh	2906vs	2910sh	2908vs	CH_2 antisymmetric str.
2902vs	2900vs	2900s		
2887m				
2870s,sh				a_1, e CH_2 sym. str.
	2861vs			
2855s	2855s	2855s	2854s	a_1, e CH_2 def.
1476vw		1477vw		
	1459w 1451w		1460m 1450m 1440sh	
1440sh				a_1, e CH_2 wag and CCH def.
1439s	1434sh	1439s		
1380vw		1380vw		
1370vw	1367w	1370vw	1352vw 1350m 1343m	a_1, e CH def.
	1346m			
1320vw	1318vw 1314vw	1320vw	1313vw	
1300w	1298m	1298br,w	1299br,w	e C—C str.
1290w	1287w			
1280w	1282m		1268vw	
1266s				e CH def
1265sh	1257vw	1264s		
1191vs			1190vw	
1186s	1186vw	1186s		a_1, e CCC bend and C—C str.
1110vw	1113w			
1104s	1105w	1103br,s		
1100sh	1099m		1102w	a_1, e C—Cl str.
1035w	1035s	1036w,br	1036m	
1030w	1026m		1000vw	
990sh				a_1 CH_2 antisymmetric def.
988sm	984w	985s	985s	
960vs	955w	958s	953w	
950w	950sh			a_1, e CH_2 antisymmetric def.
933m	931vw	932vw		
828m	825vs	829m,br	827m	
810w	810w	810w,br	809w	a_1, e CH_2 antisymmetric def.
806vw	806w 801w,sh			
772vs	770sh 768m	772vs	767m	

TABLE I (concluded)

Phase I (190 K)		Phase II (300 K)		Assignments
Raman	IR	Raman	IR	
693s	690s	694s	691m 680sh	} a_1, e C—C—C
673w	670vw		650vw 645vw	
645w	643vw	645w		} bending
476m	474w	479m,br		
453w		455w	477w	} e C—Cl bend
404w		404br,w		} Skeletal modes
360w				
355w				
339vs		339s,br		
330s				} C—C—Cl str.
221m				
215m		215m		
83vw				} Skeletal modes
65w				
64w				
60sh

FIG. 2. Raman spectra of phases I and II of 1-chloroadamantane.

ture. The dominant relaxation mechanism of the methylene and methine carbons is the dipole-dipole interaction between the ^{13}C nuclei and their attached protons, and T_1 is given by eq. [1].

$$[1] \quad 1/T_1 = (3\gamma_H^2 \gamma_C^2 h^2 / 10r_{CH}^6) \sum A_i f(\omega_H, \omega_C, \tau_i)$$

where

$$f(\omega_H, \omega_C, \tau_i) = \tau_i / [1 + (\omega_H - \omega_C)^2 \tau_i^2] + 3\tau_i / [1 + \omega_C^2 \tau_i^2] + 6\tau_i / [1 + (\omega_H + \omega_C)^2 \tau_i^2]$$

and the A_i terms are constants related to the changes in the second moments that result from the different motions. In a completely rigid lattice, or in the case of fast isotropic rotation, the ratio of the T_1 values for the methine and meth-

FIG. 3. Correlation diagram for the ordered phase of 1-chloroadamantane.

FIG. 4. ^{13}C spin-lattice relaxation times in 1-chloroadamantane.

TABLE 2. Activation energies (kJ mol^{-1}) from the temperature dependences of the ^{13}C T_1 values in 1-chloroadamantane

Carbon ^a	Phase I	Phase II
C(β)	25.8 ± 0.7	22.4 ± 1.1
C(γ)	26.7 ± 0.7	20.7 ± 1.2
C(δ)	32.1 ± 0.6	21.0 ± 1.2
Average	28.2	21.4
$^1\text{H}^b$	28.6	23.8

^aPeak assignments are from ref. 18.

^bFrom ref. 9.

ylene carbons of 1-chloroadamantane should be 2:1, or close to it. In the disordered phase I of 1-chloroadamantane, however, the order of T_1 was $C_\gamma > C_\beta > C_\delta$ and the average ratios $T_1(\gamma)/T_1(\beta)$ and $T_1(\gamma)/T_1(\delta)$ were 1.5 and 5.9, respectively. These results are almost exactly the same as those observed for phase I of 1-bromoadamantane (15), indicating that the motions modulating the relaxation process in phase I of both compounds are the same, and are not due to isotropic rotation. Furthermore, this motion may be different from that in the disordered phase of 1-fluoroadamantane since the ratios of $T_1(\gamma)/T_1(\beta)$ and $T_1(\gamma)/T_1(\delta)$ are differ-

ent, although the T_1 order for the three protonated carbons is the same. According to the neutron scattering results (10), the tumbling motion for 1-chloroadamantane in phase I is the reorientation of the molecular axis among six fourfold crystallographic [100] directions, while the molecular axis of the 1-fluoro derivative tumbles between the eight [111] directions (5). A uniaxial rotation about the molecular axis also occurs in phase I of both compounds. This fast C_3 rotation is not the dominant cause of the overall relaxation process since the combined jumps of the C—Cl axis among the six crystallographic [100] directions should average the intramolecular dipolar interaction close to zero, which is close to isotropic reorientation. If it dominated relaxation, then the order of the T_1 values would be $C_\gamma > C_\beta \approx C_\delta$, which is not the case, and, therefore, an additional motion must contribute to the relaxation. The change in second moment is reciprocally related to the T_1 minimum for each carbon, and calculations show that the second moment changes on going from a rigid lattice to a 120° jump about a C_3' axis (along the C_γ —H directions) yield the order of the T_1 minima: $C_\gamma > C_\beta > C_\delta$, which is qualitatively consistent with the experimental observations.

The activation energies for rotation for each carbon in phase I are given in Table 2. The transition to phase II occurred before the minima in T_1 were reached and, therefore, separation of the motions into the uniaxial and tumbling contributions was not possible. However, the average value is in good agreement with that obtained from ^1H NMR spin-lattice relaxation time measurements (8), but the barrier is much higher than those obtained in the neutron scattering study (9) for molecular tumbling among the [100] directions ($10.28 \text{ kJ mol}^{-1}$) and for C_3 rotation ($21.41 \text{ kJ mol}^{-1}$). Since the NMR experiment has a slower timescale than does neutron scattering, it is not surprising that the two techniques are sensitive to different motions. The activation energy for the possible C_3' rotation for 1-chloroadamantane is smaller than that for the same motion in the 1-bromo analogue (33.0 kJ mol^{-1}).

At the transition, all three carbons showed obvious discontinuities in their T_1 values. In phase II, the relaxation times have the relation: $T_1(\delta) \approx T_1(\gamma) \approx 2T_1(\beta)$ (average $T_1(\delta)/T_1(\beta) = 1.95$, $T_1(\gamma)/T_1(\beta) = 1.91$). These results indicate that the dominant motion in the ordered phase has changed to a rotation about the molecular threefold axis. Since phase II is ordered, the rotation about the C—Cl axis must be the 120° jump between crystallographically equivalent sites, without introducing any disorder. A calculation of the change of second moment from the rigid lattice to C_3 rotation yields the following T_1 minima relation: $1.6 T_1(\beta) \approx T_1(\delta) \approx T_1(\gamma)$, which is consistent with the experimental observations. By fitting the T_1 curve for each carbon, the barrier to motion was obtained, and the resulting values are listed in Table 2. The values are in good agreement with that obtained by proton T_1 measurements (8).

At the transition from phase I to phase II, the molecular tumbling is restricted, leaving rotation about the C_3 axis as the only motion responsible for relaxation. This is confirmed by the dipolar dephasing time measurements, which determine how fast a polarized carbon loses its magnetization after proton spin locking is terminated. The decay rate of the carbon signal intensity depends on the dipole-dipole interactions between the proton and carbon spins. Generally, for a molecule in a rigid lattice, dephasing is most rapid

FIG. 5. Dipolar dephased spectra of phase I.

FIG. 6. Dipolar dephased spectra of phase II.

for those carbons having directly bonded protons, such as CH and CH₂ groups, while nonprotonated carbons retain phase coherence for longer times, because there is only a small effective dipolar interaction from neighboring groups. Methyl carbons usually experience a moderate degree of C—H dipolar coupling because the internal motion tends to weaken the dipolar interactions. The decrease in signal intensity during the dephasing time is characterized by a constant T_2' .

Aleman et al. (14) have shown that fast decays, due to strong ¹³C—¹H dipolar coupling, follow a second-order exponential decay (Gaussian decay):

$$[2] \quad I_G = I_{OG} \exp(-t_{dd}^2 / 2T_{2G}'^2)$$

where I_{OG} is the signal intensity at zero time and T_{2G}' is the Gaussian decay constant. Slow decays (weak dipolar interactions) can be fitted by a first-order exponential decay (Lorentzian decay):

$$[3] \quad I_L = I_{OL} \exp(-t_{dd}/T_{2L}')$$

Sometimes, the experimental data may be resolved into multicomponent decays, such as a two-component Gaussian-Lorentzian decay, described by eq. [4].

$$[4] \quad I = I_{OG} \exp(-t_{dd}^2 / 2T_{2G}'^2) + I_{OL} \exp(-t_{dd}/T_{2L}')$$

If rapid molecular reorientation occurs in the crystal lattice, then the rate of signal decay is diminished as the motion attenuates the effective ¹³C—¹H dipolar interaction. This can be used to assign the motions occurring in different phases of the orientationally disordered solids. Figures 5 and 6 show the dipolar dephased spectra for different delay times, and Figs. 7 and 8 show the dependence of the intensities on the delay time, for 1-chloroadamantane in phases I and II, respectively. In the disordered phase, the intensities of all the α, β, γ, and δ carbons decayed very slowly and followed a Lorentzian decay. The decay constants for each carbon are given in Table 3. Although the β, γ, and δ carbons have directly attached protons, they decayed as slowly as the nonprotonated α-carbon, with similar Lorentzian decay constants, indicating that the motion modulates the three types of C—H vectors in a similar manner.

The intensities of the β, γ, and δ carbons in phase II decayed much faster than they did in phase I, indicating that the freedom of motion is drastically reduced. The relaxations of the β and γ carbons contain both Gaussian and Lorentzian components, suggesting that the motion still weakens the dipolar interaction but to a much lesser extent than in phase I. In particular, the decay of the signal for C₆ is much faster than for the other two carbons, Table 2, im-

FIG. 7. Intensities (arbitrary units) of the dipolar dephased signal versus delay time for carbon spins in phase I of 1-chloroadamantane at 283 K. Rotational echoes occur at multiples of the spinning speed.

TABLE 3. Dipolar dephasing constants (T_2' , s) for 1-chloroadamantane^a

Phase		α	β	γ	δ
I	$T_{2L'}$	2.9×10^{-3}	1.7×10^{-3}	2.1×10^{-3}	1.8×10^{-3}
	$T_{2G'}$	—	1.4×10^{-5}	1.9×10^{-5}	1.0×10^{-5}
II	I_{G0}	—	486	1029	1924
	$T_{2L'}$	—	7.1×10^{-5}	5.1×10^{-5}	—
	I_{L0}	—	658	1461	—

^aMeasured at 283 and 263 K for phases I and II, respectively.

FIG. 8. Intensities (arbitrary units) of the dipolar dephased signals versus delay time for phase II of 1-chloroadamantane at 263 K.

plying that the dipolar interaction for this carbon is still strong, and was fitted to a Gaussian decay only. The protons in the axial positions on C_8 lie parallel to the axis of rotation and, therefore, no reduction in dipolar coupling occurs as a result of the rotation. Figures 7 and 8 show clearly that, after a delay time of 50 ms, the C_8 signal has completely disappeared in phase II, but remains unchanged in phase I.

The ^{13}C spin-lattice relaxation and dipolar dephasing time behaviour of 1-chloroadamantane in phases I and II is very similar to that of phases I and III of the 1-bromo compound and we conclude that the rotational motions in these two compounds are the same, but different from the fluoroadamantane case.

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