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Dynamics of 12-Crown-4 Ether in Its LiNCS Complex As Studied by Solid-State ^{2}H NMR[†]

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Abstract: ^{2}H NMR line shape measurements and simulations were used to study large-amplitude motions of 12-crown-4 ether in its solid LiNCS complex. The overall dynamics of the molecule appear to be a composite of two motions occurring independently at slightly different rates. The first motion involves 2-site up−down flips of CH_2 groups. In the second motion the whole molecule rotates within itself such that individual $-OCH_2CH_2-$ units jump to adjacent sites. Both motions are rapid by 242 K. The first motion demonstrates that the disorder observed in the X-ray diffraction study is dynamic, whereas the second motion is diffraction invisible. There is a strong suggestion that the flip motion is actually a conversion between left- and right-handed chiral forms of the pseudo-C_4 conformation of the 12-crown-4.

Introduction

Complexes of crown ethers and their derivatives are widely recognized as model systems for some kinds of molecular recognition. The crowns can adapt their conformation for optimum complexation of the guest, a consequence of their great dynamic flexibility in solution.

In our recent studies of molecular complexes of 18-crown-6 it became apparent that in the solid state too this macrocycle has considerable motional freedom. From ^{13}C CP/MAS, ^{1}H NMR, and ^{2}H NMR studies we found evidence that the macrocycle invariably undergoes a large amplitude motion in the neighborhood of room temperature.[1−4] For the malononitrile complex [18-crown-6 · $2CH_2(CN)_2$], in which the macrocycle adopts a pseudo-D_{3d} conformation, we were able to show by means of ^{2}H NMR that the whole ring rotates within itself, each $-OCH_2CH_2-$ unit simultaneously adjusting its conformation to suit the crystallographic site being visited.[4] Such a motion, which superficially resembles that of a "merry-go-round", is essentially invisible in X-ray diffraction studies. We have since investigated solid complexes of 12-crown-4, 15-crown-5, and 21-crown-7, and all show evidence of motions. Here we report on the complex dynamics in 12-crown-4 · LiNCS.

There are numerous possible conformations for the isolated 12-crown-4 molecule,[5,6] but in the solid state only a few of these conformations have been observed so far.[7−16] In Li$^+$ complexes only one conformation, "C_4", seems to be favored.[10−16] "C_4" is frequently used lightly to describe the group of structures based on an idealized molecule with true C_4 symmetry,[10] though in most observed cases there are distortions[11−16] and pseudo-C_4 is a more appropriate name. In this conformation the four O atoms form a plane with the CH_2 groups on the one side and the Li$^+$ coordinated on the other side, Figure 1. In each OCH_2-CH_2- group one C is closer to the O atom plane (we will refer to this as the "up" position) and the second C is further from the O atom plane ("down" position). For pseudo-C_4 symmetry if one goes around the macrocyclic chain from one O atom the first carbon is down and the next up, a conformation which repeats in the next three OCC units (u d u d u d u d). Note that this is a chiral form with a mirror image equivalent, Figure 1. The crystal structure of the 12-crown-4 · LiNCS complex[11] is very interesting in that it has a mirror plane passing through

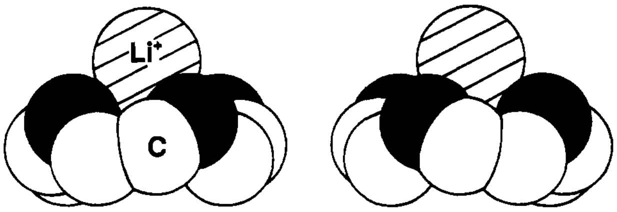

Figure 1. Schematic figure of the C and O atoms of 12-crown-4 coordinated chirally to an Li$^+$ atom.

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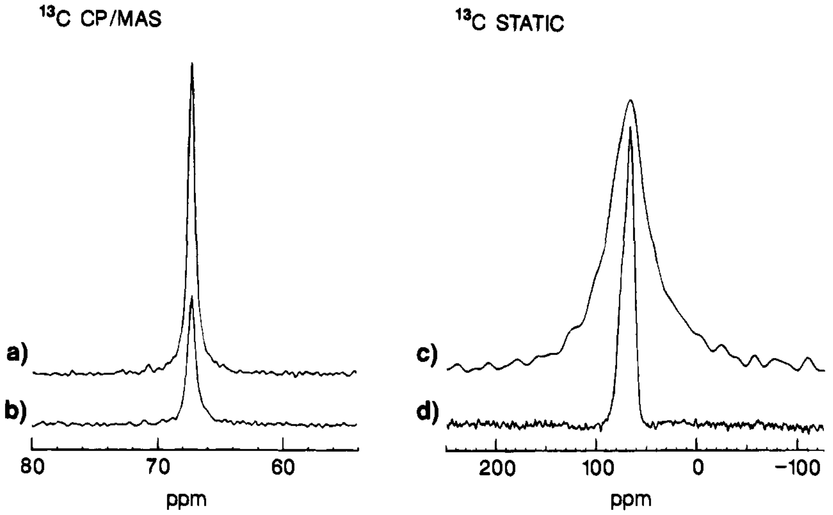

Figure 2. ^{13}C NMR spectra of the CH_2 carbon region of 12-crown-4 • LiNCS: CP/MAS spectra at 297 K (a) normal and (b) dipolar dephased; static spectra for (c) normal ^{13}C with ^1H decoupling at 190 K and (d) CP at 301 K.

two of the O atoms and the LiNCS atoms. This mirror plane is associated with a disorder which manifests itself in the form of two positions (up and down) for each CH_2 group. The atomic positions are consistent with overlap of the two chiral pseudo-C_4 conformations. The disorder could be either static, where equal numbers of left- and right-handed molecules give the required spatial average, or dynamic, where each molecule flips between left- and right-handed versions. We carried out ^2H NMR studies of the dynamics of the host 12-crown-4, with a view to determine first whether there is a concerted reorientation of the whole molecule similar to that in 18-crown-6 and second the nature of the disorder and its possible influence on the overall motions.

Experimental Section

12-Crown-4-d_4 was prepared as follows: A 1-L three-necked round-bottom flask was charged with *tert*-butyl alcohol (450 mL) and lithium metal (1.6 g, 0.23 mol). This mixture was stirred mechanically for 1 h. Ethylene glycol-d_4 (98 atom %, MSD Isotopes) (4.46 g, 0.073 mol) was added dropwise causing the formation of a white suspension. Lithium bromide (6.34 g, 0.073 mol) and 1,8-dichloro-3,6-dioxaoctane (13.75 g, 0.073 mol) were added in succession and the mixture was refluxed for 12 days. After a few hours of refluxing, the entire contents formed a thick white suspension which remained for 5 days. Subsequently a translucent beige solution formed. After cooling, the solution was neutralized with 3 M HCl and the solvent was removed via distillation at reduced pressure. The residue was transferred to a separating funnel containing 500 mL of distilled water and subsequently extracted with dichloromethane (4 x 125 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed by rotoevaporation. The remaining brown oily residue was distilled under vacuum (0.5 mmHg) to give 3.62 g (28.1%) of 12-crown-4-d_4, bp 65−70 °C (reported bp for 12-crown-4 is 67−70 °C at 0.5 mmHg pressure[17]). In the product thus formed one of the four $-OCH_2CH_2-$ groups becomes $-OCD_2CD_2-$.

12-Crown-4-d_4 • LiNCS was prepared as follows: 12-Crown-4-d_4 (1.0 g, 5.6 mmol) and LiNCS (0.37 g, 5.6 mmol) were combined and dissolved in 5 mL of methanol. The solution was evaporated to a volume of 2.5 mL and then stored overnight in a freezer at −10 °C. This yielded 0.93 g (68%) of colorless crystals, mp 249−251 °C (reported mp for 12-crown-4 • LiNCS is 250−252 °C[11]).

^2H NMR powder spectra were recorded on a Bruker CXP-180 spectrometer at 27.63 MHz as a function of temperature by using a variable-temperature N_2 gas-flow probe with a Bruker B-VT-1000 temperature controller. A phase-alternated quadrupole echo pulse sequence[18] was used with a delay time of 35 μs between X and Y pulses of 2.6−3.0 μs. ^{13}C CP/MAS and static NMR spectra were obtained at 45.26 MHz using a Doty Scientific Inc. 7 mm probe.

^2H NMR Background

Since the bulk of this paper concerns the analysis of the effects of motion on ^2H NMR line shapes it is necessary to give a very brief description of the underlying principles. All the basic theory has been described in detail elsewhere,[19−24] and we will follow the same treatment as before.[4] Briefly, ^2H ($I = 1$) NMR in solids is dominated by a perturbation of the Zeeman interaction by the quadrupole coupling tensor which itself arises from the interaction of the nuclear quadrupole moment with the electric field gradient around the nucleus. The ^2H powder line shape, which arises from the summation of resonance line pairs for a distribution over all crystallite orientations, has either 2 or 3 pairs of characteristic features (edges, shoulders, and peaks) separated by frequencies

$$\begin{aligned}\Delta\nu_{zz} &= 3\chi/2 \\ \Delta\nu_{yy} &= 3\chi(1+\eta)/4 \qquad (1) \\ \Delta\nu_{xx} &= 3\chi(1-\eta)/4\end{aligned}$$

where χ is the quadrupole coupling constant ($=e^2qQ/h$) in hertz and the asymmetry parameter η is $(\Delta\nu_{yy} - \Delta\nu_{xx})/\Delta\nu_{zz}$. The $\Delta\nu_{ii}$ are proportional to the principal axis components of the effective quadrupole coupling tensor, but information regarding signs of these is lost.

Molecular motion at sufficiently high rates can cause changes in the ^2H NMR line shape. Differing degrees of line shape averaging are observed depending on the rate of reorientation and the orientations of the principal axes of the EFG tensor relative to the rotation axis. In the fast motion limit (reorientation rates about 10^7 jumps/s or faster) analytical expressions for the line shapes are relatively easy to obtain:[20,21,24] The

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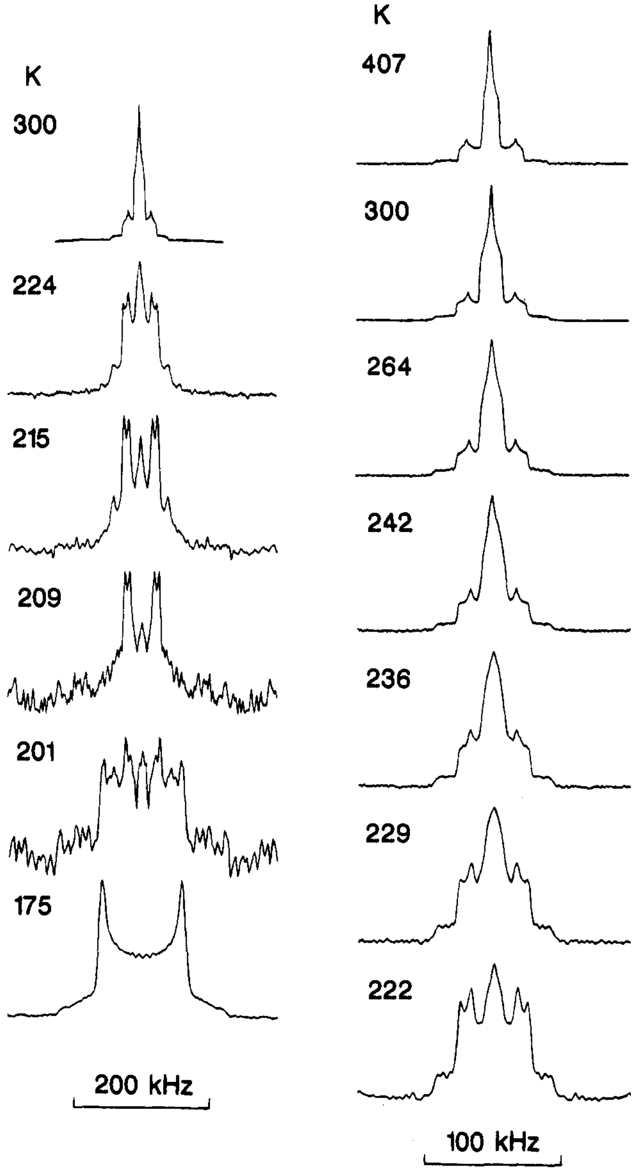

Figure 3. ^2H NMR line shapes of 12-crown-4-d_4 • LiNCS as a function of temperature. Note the 2-fold expansion of the frequency scale in the right-hand column.

orientation of the tensor must first be described in a final reference frame in terms of the Euler angles

$$\mathbf{V}(\alpha,\beta,\gamma) = \mathbf{R}\mathbf{V}_{\text{pas}}\mathbf{R}^{-1} \tag{2}$$

where **R** is the Euler angle rotation matrix describing the coordinate transformation and $\mathbf{V}_{\text{pas}}$ is the tensor in its principal axis system. The fast motion line shape is then given by an effective tensor which is the population weighted average of the tensor components in the final frame for all the sites (orientations) visited during the motion.

$$\mathbf{V}_{\text{eff}} = \sum_{i=1,n} \mathbf{V}_i(\alpha,\beta,\gamma)p_i \Big/ \sum_{i=1,n} p_i \tag{3}$$

where p_i is the population factor of site i.

Intermediate rate line shapes depend on the specific rate of motion and the experimental details (e.g. on the echo delay time) and have to be calculated numerically. Methods for doing this are well-established.[20-23]

Results and Discussion

^{13}C NMR Spectra. The ^{13}C CP/MAS NMR spectrum at room temperature shows a single isotropic resonance at 67.3 ppm, with no spinning sidebands, Figure 2. The same peak appears under dipolar dephasing conditions with about 40% residual intensity. This is clear evidence of motion; the carbons all have two attached H atoms, and without motion the ^{13}C resonance should be dephased by coupling to the ^1H nuclei during the interruption of decoupling and disappear from the spectrum. Further evidence for dynamic processes comes from a comparison of the non-spinning but ^1H decoupled ^{13}C NMR line widths at room temperature (~14 ppm) and at 177 K (~72 ppm), indicating dynamic averaging of chemical shift anisotropy.

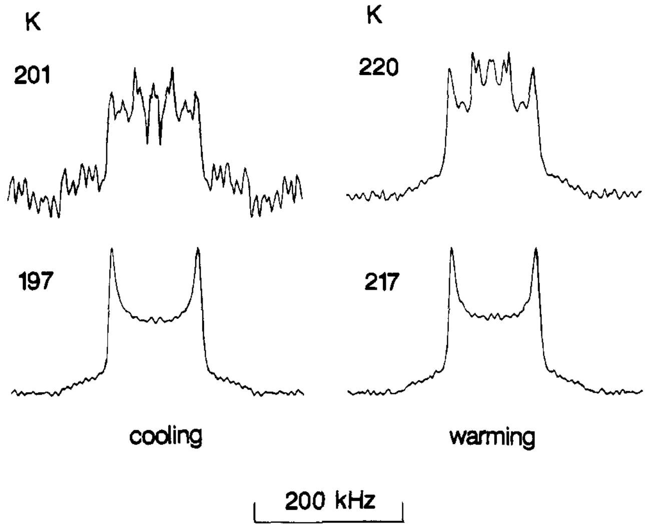

Figure 4. ^2H NMR line shapes of 12-crown-4-d_4 • LiNCS in the region of the phase transition, showing hysteresis on cooling and warming. The spectrum at 220 K is a mixture of both phases obtained before complete conversion to the high-temperature phase. The much reduced signal/noise ratio of the spectrum at 201 K is due to the dynamic processes.

Table 1. Observed ^2H Quadrupole Coupling Constants (χ_{eff}) and Asymmetry Parameters (η_{eff})

complex	dynamic state[a]	temp, K	χ_{eff}, kHz	η_{eff}
12-crown-4-d_4 • LiNCS	f.m.l.	407[b]	55.54	0.141
			8.382	1
	f.m.l.	300	56.84	0.206
			11.48	1
	f.m.l.	242	56.97	0.226
			12.02	1
	static	218	158.9	0
	static	175	166.7	0
18-crown-6-d_4 • $2CH_2(CN)_2$ (ref 4)	static	198	164.1	0.071

[a] f.m.l. = fast motion limit. [b] The two sets of parameters given for 407, 300, and 247 K refer to the two separate equal intensity patterns which make up the total line shape.

^2H NMR Spectra. The ^2H NMR spectra of 12-crown-4-d_4 • LiNCS as a function of temperature are shown in Figures 3 and 4, and Table 1 lists the measured effective χ and η for the static and fast motion limit line shapes. Also included in Table 1 for comparison are the values for the 18-crown-6 • $2CH_2(CN)_2$ complex.[4] Very sudden changes in the line shape occur between 201 and 197 K on cooling and between 217 and 220 K on warming, strongly indicative of a phase transition with hysteresis. This was confirmed by DSC on the fully protonated material, Figure 5 (cooling: onset 191 K, peak 189 K; warming: onset 216 K, peak 219 K). The occurrence of a phase transition is not surprising, as Groth reported disintegration of his single crystals when he attempted to cool them to low temperatures.[11]

Below the phase transition the line shapes correspond to an essentially static 12-crown-4, except for librational or small

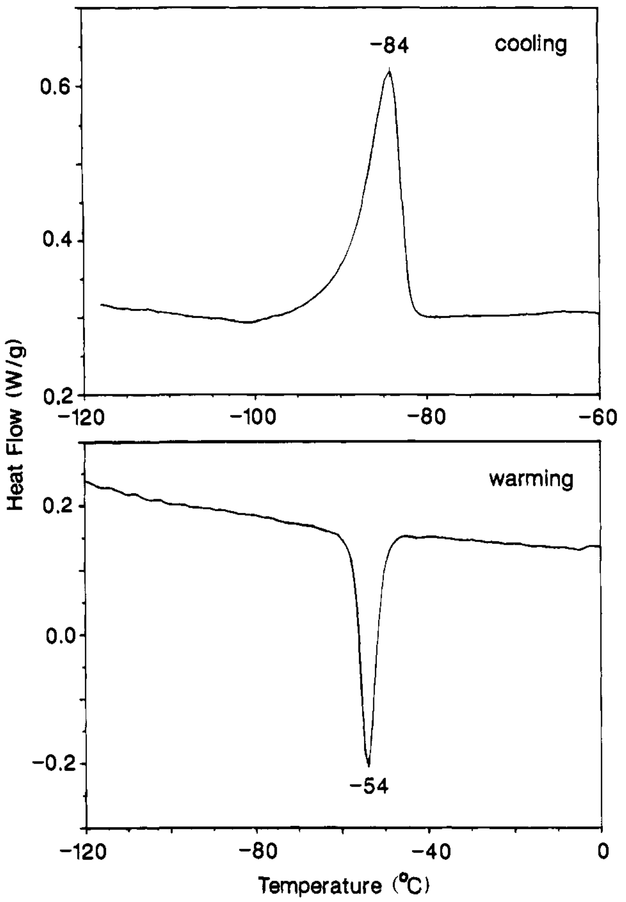

Figure 5. DSC scans of 12-crown-4·LiNCS on cooling (top) and warming (bottom).

amplitude flexing motions which produce a small amount of narrowing as temperature increases (see Table 1). The absence of any discernible asymmetry in the static line shapes for the 12-crown-4 complex may be a consequence of the crystallographic inequivalence of all the C—D bonds leading to a slight distribution in quadrupole coupling parameters. Above the transition, dynamic processes in the intermediate rate regime are evident, in that the line shapes undergo pronounced changes in shape and intensity as a function of temperature. Above 242 K these changes have ceased and the line shapes correspond to the fast motion limit. An additional small decrease in the line width but without any change in shape as temperature increases further is apparent. It is very interesting that the fast motion limit spectrum is a superposition of *two* distinct and non-axially anisotropic line shapes, of equal integrated intensity and much narrower than the static line shape.

From the line shape parameters we can obtain the components of the static and averaged quadrupole coupling tensors and proceed to find dynamic models consistent with the data.

Analysis and Model

First, it is necessary to define the orientations of the principal tensor components for all the D atom sites. In the case of C—D bonds the principal *ZZ* axis of the electric field gadient tensor is, to a first approximation, oriented along the bond vector, and in the present case we can make a reasonable assumption that the *YY* or *XX* component of the tensor will be perpendicular to the CD_2 plane. The exact geometry of the C—D bonds is not known because the diffraction does not permit good refinement of the H positions (in fact Groth calculated the H positions but did not refine them,[11] apparently with tetrahedral HCH angles and bond lengths of 1 Å). Consequently we inserted 2 H atoms for each carbon in a plane at right angles to the O—C—C plane and equally displaced on either side of the OCC bisector, with the HCH angle initially at 101°. We then calculated the Euler angles to transform the ^2H quadrupole coupling tensors into the chosen reference frame, defined by the pseudo-4-fold axis and the mirror plane (according to eq 2). Because the static tensor appears to have axial symmetry, the *XX* and *YY* components are equal and the Euler angle α is redundant (=0). These angles were then used in calculations (using eq 3) of the fast motion limit line shapes for exchange between various sets of sites. In all calculations we used the parameters obtained for the low-temperature phase at 218 K on warming as representative of the "static" line shape. It is a reasonable assumption that the equivalent parameters for the room temperature phase would be little different. In the present case the averaged tensors were not diagonal in the reference frame defined above.

The fact that the fast motion limit spectrum is a superposition of only two distinct and non-axially anisotropic line shapes indicates the following: (a) All the deuterons are involved in the dynamics. (b) Since there is only one molecule in the asymmetric unit, there must be two distinct groups of exchanging sites for each molecule. (c) The motion is not a simple rotation about an *n*-fold ($n \geq 3$) axis, since this would give an axially symmetric line shape. This is consistent with the absence of a true axis of symmetry within the molecule.

In searching for a plausible dynamic model to explain the experimental results we are influenced to some extent by the behavior of 18-crown-6 discussed previously, which suggests that there is a certain ease for the molecule to reorientate within itself. However, the strongest guide is that any model must be consistent with the structural information. Furthermore, one must take into consideration the topology of the macrocycle and the relative strains of different conformations. Fortunately this immediately restricts the number of possibilities.

With 8 C atoms in the molecule, each with two crystallographic positions, there are 16 C sites and 32 H (or D) sites. There can be no physical exchange between the four H positions *within* each $-OCH_2CH_2-$ unit, thus the 32 possible H sites group into 4 sets of 8 mutually exchangeable sites. Each group of 8 consists of the up and down sites in each of the four $-OCH_2CH_2-$ units.

The observation that there are only two superimposed averaged components to the line shape leads to the conclusion that the four sets of sites have grouped into equivalent pairs, through either symmetry or dynamics or both. This also excludes the two simplest motions we can consider:

(a) If the pseudo-C_4 molecule simply reorientates into itself, i.e. (O—C—C)1 moves into the position of (O—C—C)2 and so on, then there must always be four sets of sites which are exchanging and we should expect four overlapped dynamically averaged line shapes (simulated line shape based on such a motion shown in Figure 7, top right hand corner). The molecule with opposite chirality would produce the same result.

(b) If the only motions were up/down flips of CH_2 groups there would be 16 pairs of exchanging sites. Pairs of these would be equivalent because of the mirror plane, resulting in a superposition of eight distinct averaged line shapes (Figure 7, bottom left hand corner).

Two other models which were considered are as follows:

(c) A motion similar to that in D_{3d} 18-crown-6[4] would involve reorientation from one $-OCH_2CH_2-$ site to the next but with a simultaneous flip of the CH_2 groups. Of course this also implies a starting conformation different from pseudo-C_4 (i.e. in terms of C atom positions around the macrocycle: u d d u u d d u), which to conform to the atomic positions of the crystal structure would be highly strained. While this model is therefore

Table 2. Euler Angles Defining the Orientations Visited by the Two Types of Exchanging ^{2}H

α (deg)	β (deg)	γ (deg)
Set 1 ($V_{zz} = 85.37$; $V_{yy} = -52.31$; $V_{xx} = -33.06$)[a]		
0	38.23	121.21
0	52.65	1.497
0	27.65	225.19
0	44.02	268.38
0	28.06	312.87
0	45.37	174.17
0	29.19	26.11
0	59.61	98.43
Set 2 ($V_{zz} = V_{yy} = 18$; $V_{xx} = 0$)[a]		
0	68.43	275.33
0	41.87	59.80
0	79.24	12.48
0	49.33	321.66
0	78.78	102.95
0	45.91	225.53
0	74.89	188.95
0	35.04	157.06

[a] Averaged tensor components (kHz).

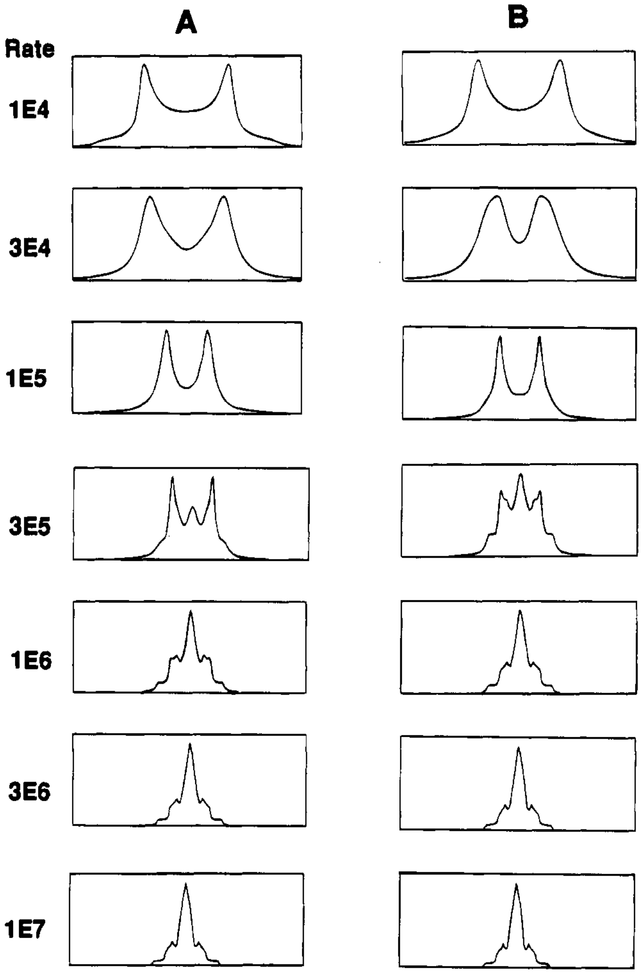

Figure 6. Simulated ^{2}H NMR quadrupole echo line shapes for (A) rotational jumps to adjacent sites with the possibility of simultaneous flips (mechanism (ii)) and (B) jumps among all of the eight sites available to each deuteron (mechanism (i)).

not considered too likely to begin with, it can definitely be ruled out on the basis that it would lead to four overlapped averaged line shapes rather than two.

(d) A combination of the motions in models (a) and (b) above allows each D to visit all eight sites within its set, and, moreover, two pairs of sets become equivalent.

Model (d) was found to be the only one which was able to reproduce the experimental fast motion limit line shape (at 242 K) fairly closely using the initial Euler angle sets described above. By adjusting all the Euler angles by small amounts it was possible to find an exact match. The final sets of Euler angles used are given in Table 2. The DCD bond angles corresponding to these range from 98.83 to 103.24°, close to the angle of ~100° which was found to give the best fit in the study of 18-crown-6 • $2CH_2(CN)_2$.[4] Note that these sets do not give a unique solution; because there are so many angles involved, many other similar sets may give the same exact match. However, they are a very reasonable and representative solution.

The analysis of the fast motion limit line shape above only tells us which sets of sites are in rapid exchange. Unfortunately it does not indicate *how* the exchange takes place, e.g. it does not allow a distinction between a mechanism where the flip and rotational jump motions occur simultaneously or one where they occur independently at different rates. We must look to subtle effects in the intermediate rate line shapes to help distinguish these different possibilities: Simulations of quadrupole echo line shapes were performed using a considerably modified version of the program of Vega and Luz.[23] Calculations for the two sets of sites were performed separately and then added together with intensities weighted by their echo amplitudes. Kinetic exchange matrices were constructed for three reasonable mechanisms: (i) exchange among all eight sites at equal rates, which in effect allows combined jump and flip motions, (ii) exchange only between adjacent $-OCH_2CH_2-$ sites with the possibility of a simultaneous flip, and (iii) jumps between adjacent $-OCH_2CH_2-$ sites at one rate and flips between up and down C positions at a different rate. If the rate for one process or the other in (iii) is made very small then the situation reduces to case (a) or (b) described above in the fast motion limit line shape analysis.

The results are shown in Figures 6–8, from which it can be seen that simulations based on mechanism (iii) (Figures 7 and 8) can more closely match the experimental line shapes. Mechanisms (i) and (ii) are not able to simulate the line shapes at 209 and 215 K, particularly with respect to the pair of doublets which should have roughly equal intensity, also the growth of intensity in the central line seems to outpace the changes in the broader component when compared with the experimental line shapes. It is rather unfortunate that the temperature of the phase transition is such that line shapes for the lower end of the range of jump rates are unattainable. However, from the comparison between simulation (iii) and experiment it seems that the flip motion occurs independently at a slightly faster rate than rotational jumps; for instance the line shape is simulated well with a rotation rate of 5.6 × 10^5 to 1 × 10^6 jumps/s and the faster flip rate of 3 × 10^6 flips/s at 224 K and by a rotation rate of 1.8 × 10^5 to 3 × 10^5 jumps/s and a flip rate of 1 × 10^6 to 1.8 × 10^6 flips/s at 209 K. The approximate region in the 2-dimensional rate plot followed by the combined motion is indicated in Figure 8. The rapid decrease in experimental signal-to-noise ratio from 224 down to 201 K is also reflected very well in the echo amplitudes of the simulated spectra, which reach a minimum in the region where the rates for both motions are about 1 × 10^5 jumps (or flips)/s.

Considering the assumptions entailed in getting this far, the comparison between simulation and experiment is remarkably good, and while there may not be a completely unique solution the model derived is eminently plausible.

The ^{2}H NMR line shapes are only sensitive to motions of individual C–D bonds, and consequently they do not provide information about whether motion of the different CD_2 groups is correlated, i.e. we cannot distinguish between independent

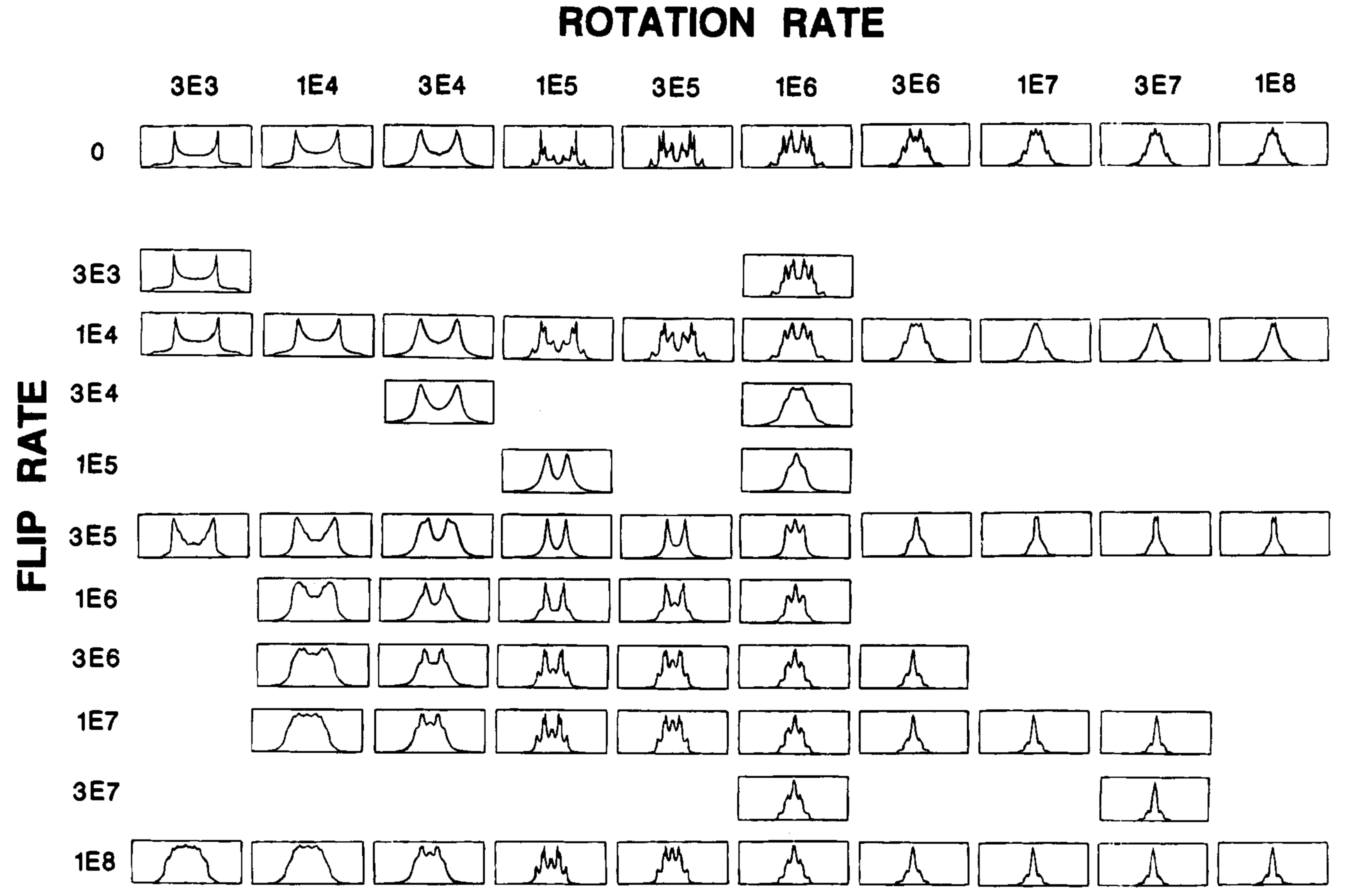

Figure 7. Partial matrix of simulated ^{2}H NMR quadrupole echo line shapes as a function of pseudo-4-fold jump rate to adjacent $-OCH_2CH_2-$ sites on the horizontal axis and flip rate on the vertical axis (mechanism (iii)).

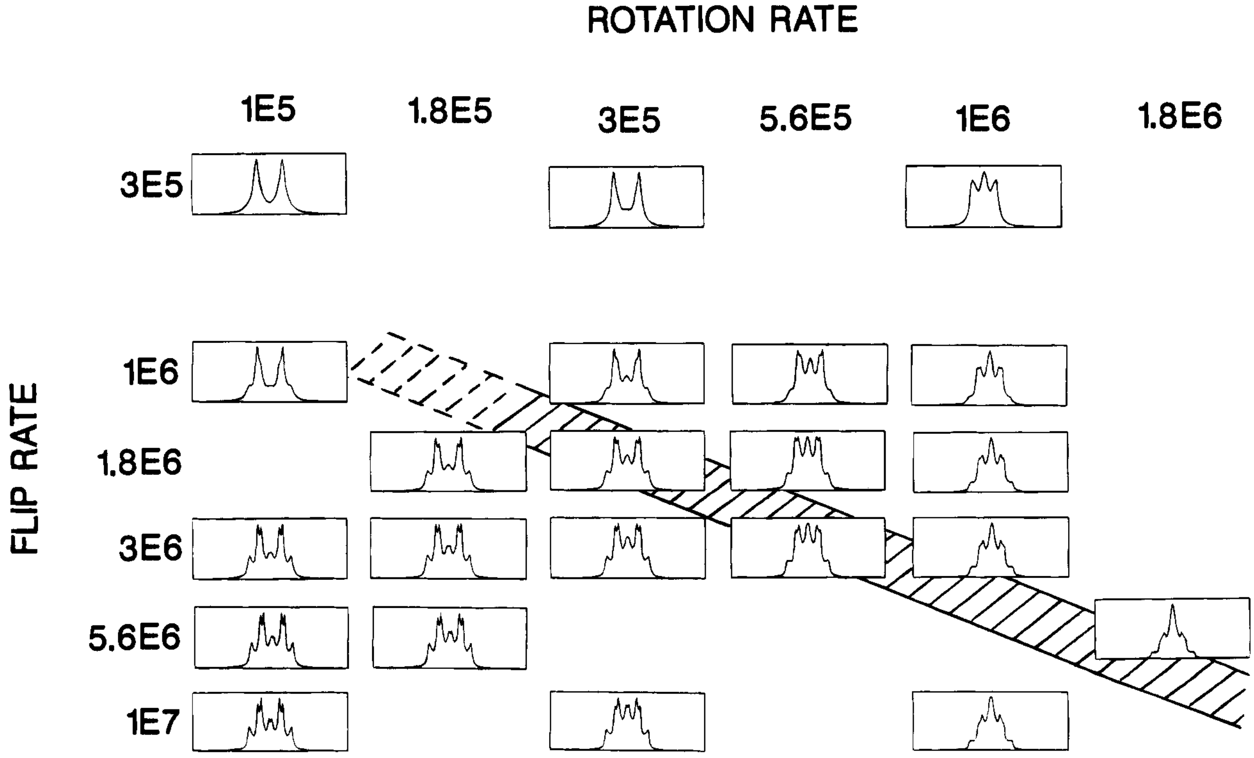

Figure 8. Expanded partial matrix of simulated ^{2}H NMR quadrupole echo line shapes as a function of pseudo-4-fold jump rate and flip rates (mechanism (iii)) in the region which most closely matches the observed line shapes. The shaded area indicates roughly the region of jump and flip rate combinations where the simulations most closely resemble the experimental line shapes.

CD_2 flips, correlated flips of the 2 CD_2 groups in one OCD_2-CD_2- unit, or whether all CD_2/CH_2 groups flip at the same time in a switch between the two chiral forms of the pseudo-C_4 conformation.

However, it is not possible to flip just one CH_2 group without affecting the rest of the molecule, since this would create some very unfavorable C—O—C and O—C—C bond angles. At the very least the neighboring CH_2 should also flip to relieve the strain. This inverted CH_2CH_2 unit will produce some distortion at the adjacent O atoms which in turn would promote flips of the next groups in a ripple effect. All this could take place in a time very short compared to the time between flips. Alternatively, it might be energetically more favorable for all the groups in the ring to flip in one concerted motion. So it is quite possible that the relief of strain might be a driving force for concerted flips of the whole molecule between left- and right-handed forms.

Conclusion

The ^{13}C and ^{2}H NMR line shape studies provide very clear evidence that in 12-crown-4·LiNCS the crown molecule undergoes motion which is rapid on the NMR time scale somewhat below room temperature. By a process of elimination we have arrived at a very plausible dynamic model involving two independent motions: up/down flips of CH_2 groups and pseudo-4-fold rotational jumps of the ring. The picture developed from the NMR results is entirely consistent with the crystal structure data and demonstrates that the disorder present is dynamic. Consideration of the conformational strains involved suggests that concerted flips between the two chiral forms of the molecule may be occurring.

The dynamics of 12-crown-4 in this complex are more complicated than the merry-go-round motion observed in 18-crown-6·$2CH_2(CN)_2$, though there are obvious similarities, and it is still remarkable that motion in these large macrocycles is so facile.

Finally, to end on a speculative note, we would like to suggest that the freezing out of the flip motion might drive the phase transition on cooling, since the material would have to form a racemic crystal or separate left- and right-handed crystals.

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