Macrocycle Reorientation in Solid 18-Crown-6 Complexes detected by 1H and 13C N.M.R. Spectroscopy

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Solid state 1H and 13C n.m.r. spectra of 18-crown-6 complexes indicate reorientational motions of the macrocyclic ether, at or near room temperature, in contrast with apparently static X-ray structures.

Little is known about the stereochemical dynamics of 18-crown-6 and its complexes in the solid state, although, in solution, a single 13C or 1H n.m.r. resonance is observed down to 143 K,[1] owing to rapid conformational averaging. X-Ray crystal structure data show these materials to have well-defined, locked conformations at ambient temperatures.[2] It was surprising, therefore, to find, in earlier work, that solid state 13C cross polarisation magic angle spinning (c.p. m.a.s.) n.m.r. spectra obtained at room temperature consisted of single, *broad* lines.[3] Spectra of solid 18-crown-6, and its NaCNS·H₂O and KCNS complexes at *low* temperatures showed fine structure consistent with locked conformations. Line multiplicities were interpreted in terms of the symmetry of the macrocycle as dictated by the content of the crystal asymmetric unit, and chemical shifts were rationalised in terms of the local stereochemistry. The motion responsible for the conformational averaging at room temperature was then identified tentatively as torsional angle averaging due to pseudo-rotational and vibrational motion. Based on additional results we now propose a motional model to account for the apparently divergent pictures resulting from crystallographic and n.m.r. data.

Examination of 13C c.p. m.a.s. n.m.r. spectra of several 18-crown-6 complexes showed that the ether carbon line was essentially invisible at room temperature and that for other complexes the spectrum was very broad. Temperature dependent c.p. m.a.s. n.m.r. studies showed that for many 18-crown-6 complexes the macrocycle resonance goes through a 'fade-out' region, where the line becomes so broad as to be unobservable (see Table 1). This is illustrated for the malononitrile complex, where the fade-out occurs at ~250 K, Figure 1(b). Any fine structure observed at low temperatures collapses before fade-out occurs. In those cases where temperatures well above the fade-out region can be reached, the crown ether spectrum consists of a single sharp resonance; *i.e.* the chemical shift differences seen in the low temperature spectra have been averaged by exchange.

Rothwell *et al.*[4,5] have identified two mechanisms whereby a fade-out is expected. The first occurs for nuclei which have, as their main static broadening interaction, the anisotropic chemical shift. In this instance, incoherent averaging due to random molecular motion interferes with coherent averaging produced by slow magic angle spinning, and maximum broadening occurs when the motional jump rate and the
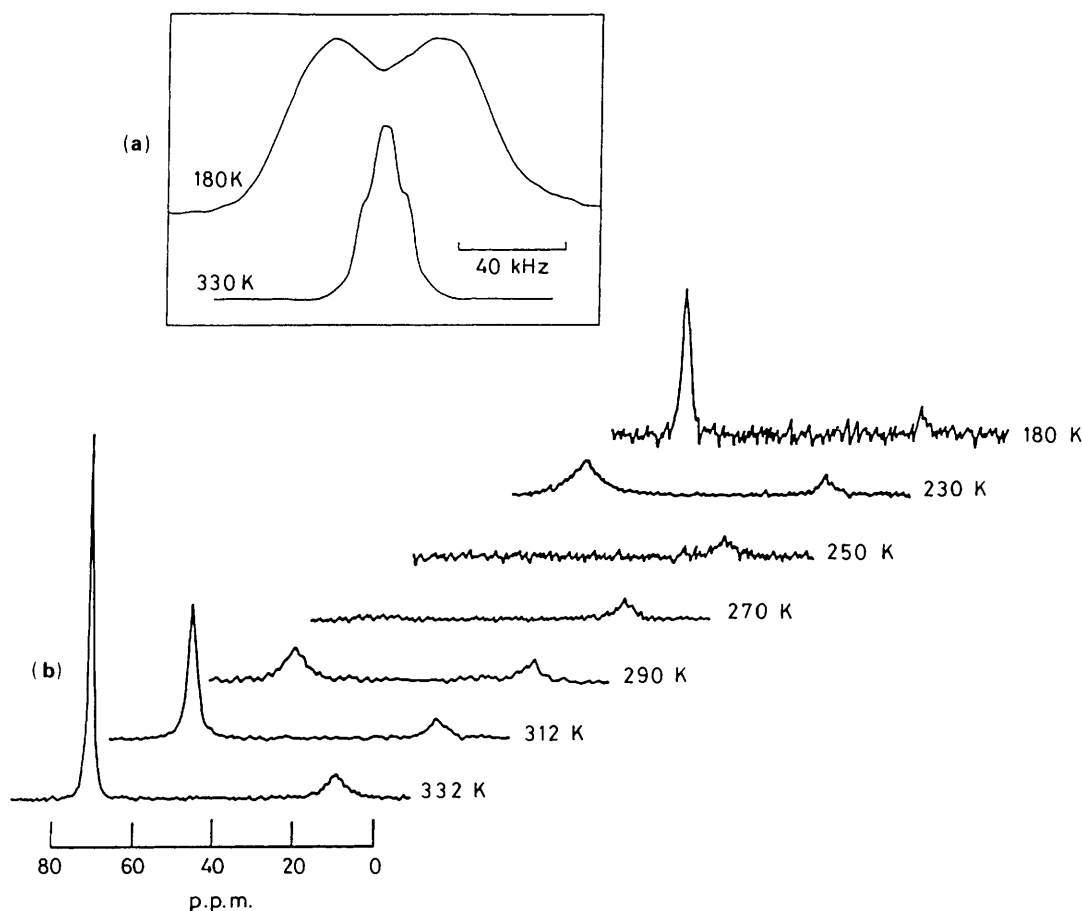
Figure 1. (a) ^1H Static n.m.r. spectra (180 MHz) and (b) ^{13}C c.p. m.a.s. n.m.r. spectra (45.28 MHz), of the 2:1 complex of malononitrile with 18-crown-6 as a function of temperature. In (b) only the CH_2 resonances are shown and the spectra are normalized on the $CH_2(CN)_2$ intensity.

spinning rate are equal. The second mechanism occurs for nuclei for which the principal line broadening is due to heteronuclear dipolar coupling. Excess line broadening occurs when incoherent averaging due to the molecular motion interferes with the coherent averaging of the decoupling field. For CH_2 groups, dipolar coupling is by far the stronger interaction (60 vs. 2—3 kHz for the anisotropic chemical shift), and under conditions of relatively rapid spinning (3–4 kHz) we take the second mechanism to be the operating source of line broadening. Maximum broadening then occurs when the motional correlation time is about equal to the inverse of the decoupling field amplitude, $\tau_c = 1/(2\pi\gamma H_1) \sim 2.5 \times 10^{-6}$ s, in our case. The main conclusion, therefore, is that a relatively slow, large amplitude motion, with definite correlation time, occurs for the 18-crown-6 macrocycles.

Other evidence for such motion comes from examination of the ^{13}C lineshape for static samples in the slow and fast motion limits. The low temperature lineshape is a powder pattern with a near-axial chemical shift anisotropy, $\Delta\sigma \approx 55$ p.p.m. The high temperature spectrum is again near-axial but the sign of the anisotropy is reversed, $\Delta\sigma \approx -25$ p.p.m. These lineshapes are not as sharp as one might expect for a single type of CH_2 carbon, as a number of inequivalent carbons may contribute. However, the change in the shielding pattern means that reorientational motions must be taking place.

The third piece of evidence comes from the static ^1H spectrum, Figure 1(a). At low temperatures the half-width of

Table 1. Summary of complexes studied, ^{13}C n.m.r. 'fade-out' temperatures and estimated activation energies.

18-Crown-6 complex	Ring pseudo-symmetry	Fade-out temperature /K	Activation energy /kJ mol^{-1}
2:1			
Phenylsulphonamide	C_i	295	45.7
1:1			
Phenylsulphonamide	D_{3d}	295	45.7
Dithio-oxamide	C_i	350	54.3
Nitromethane	D_{3d}	295	45.7
Formamide	D_{3d}	350	54.3
Malononitrile	D_{3d}	250	38.8
Perchloric acid	D_{3d}*a	205	31.8
Dimethyl sulphone	D_{3d}	340	52.7
N-Methylthiourea	C_i+D_{3d}	340	52.7
Uncomplexed 18-crown-6	C_i	>295	>45.7

a Assumed from narrow chemical shift range at low temperature.

the spectrum is about 80 kHz whereas at high temperatures the width is about 20 kHz. This change represents quite a drastic reduction in the strength of the ^1H–^1H dipolar coupling, again characteristic of considerable motion.

We therefore require a model which allows a large

amplitude motion, consistent with the n.m.r. data while at the same time preserving the X-ray crystallographic conformation of the 18-crown-6. The motion must be sufficient to cause an averaging of dipolar couplings (^{13}C–^1H and ^1H–^1H) and ^{13}C chemical shift differences, and reduce the width and change the sign of the chemical shift anisotropy. The only motion possible is one where the entire macrocycle reorientates such that O–CH_2CH_2–O units exchange positions around the ring. Each unit must simultaneously readjust to fit the local conformation of each site visited, thereby keeping the crystallographic structure unchanged. (The motion envisaged is analogous to a small cyclic molecule undergoing simultaneous reorientation and ring puckering motions.) The presence of an explicit symmetry axis for rotation does not seem to be important as the motion takes place for 18-crown-6 complexes having either the pseudo-D_{3d} symmetry or C_i symmetry (see Table 1). Work is in progress to produce deuteriated 18-crown-6 and then obtain more specific information on details of the motion from ^2H n.m.r. lineshapes.

A rough estimate of the activation energy for the motion can be obtained if the ^{13}C spectrum fade-out region ($\tau_c \sim 2.5 \times 10^{-6}$ s) is considered to correspond roughly to the region of ^1H–^1H motional narrowing ($\tau_c \sim 10^{-6}$ s). Application of the Waugh–Fedin approximation[6] ($E_a \sim 155\ T_c$ J/mol, where in our case T_c = fade-out temperature) then gives the activation energies, Table 1.

It is initially rather surprising that such a large ring should so easily undergo reorientation at ambient temperatures, but the solution n.m.r. studies have already indicated the very flexible nature of the 18-crown-6 ring, and perhaps concerted conformational changes during reorientation conspire to keep the overall potential barrier reasonably low in the solids.

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