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SOLID PHASE CARBON-13 NMR STUDIES OF DICYCLOHEXYL-18-CROWN-6 ETHERS AND SOME ALKALI METAL PHENOXIDE COMPLEXES

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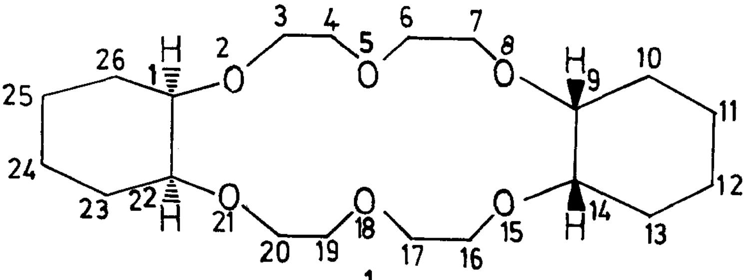
Abstract: From C-13 CPMAS spectra, the asymmetric units in the crystalline state of a number of title species have been determined. Results are compared with available x-ray data and liquid phase C-13 spectra.

Recently the details of the dynamic stereochemistry of the cis-syn-cis and cis-anti-cis isomers of dicyclohexano-18-crown-6 ethers and their sodium and potassium phenoxide complexes in solution have been elucidated (1,2). In all cases rapid conformational averaging at room temperature leads to the observation of only five C-13 signals for the macrocyclic ligand and four C-13 signals for the phenoxide moiety. With the present interest in the conformational properties of "host-guest" complexes in the solid state, the application of high resolution C-13 CPMAS techniques to this area seems appropriate.

For the cis-anti-cis isomer (1) below, the x-ray structure (3) of the B' polymorph (4) has been reported. The crystal is found to possess a centre of symmetry.



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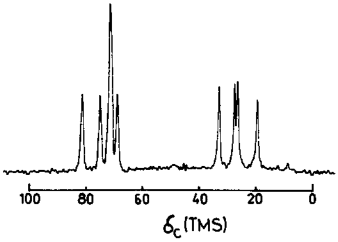
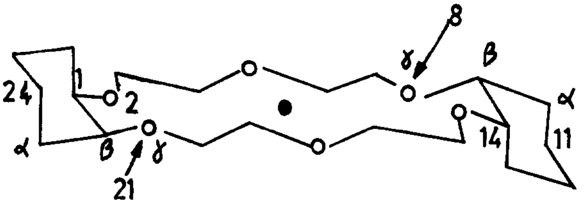
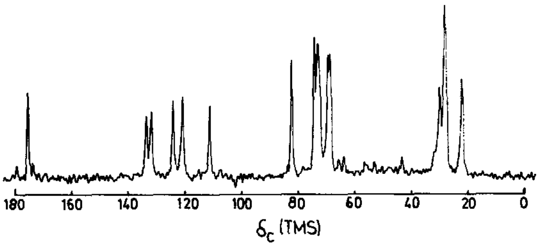
The C-13 CPMAS (5) spectrum below, shows four resonances of nearly equal intensity in the chemical shift range of 18-35 ppm, arising from the non-oxygenated carbons C10-13 and C23-26. Oxygenated carbon resonances appear in the range from 68-82 ppm. In the latter region the intensities are in the ratio of 1:3:1:1, with two instances of accidental resonance overlap giving rise to the intensity 3 line (6).



This spectrum is consistent with a conformationally locked crown ether structure in which there is a centre of symmetry (below) and the asymmetric unit is half the molecule. In such a structure one would expect to observe ten C-13 resonances in the absence of any accidental overlap. Of the four non-oxygenated carbons, the C-11,24 symmetry equivalent pair is expected to appear at highest field, *ca.* 20 ppm, due to the *gauche*-gamma relationship with the axial oxygen atoms at the 8,21 positions respectively (1). In the oxygenated carbon region, the C-1,14 pair is expected to resonate at lowest field, *ca.* 82 ppm, due the influence of the directly bonded equatorial oxygens at sites 2 and 15 respectively. These resonance positions are within 1-2 ppm of those found in solution at a temperature of 183K where ring inversion is slow on the NMR timescale (1).



The C-13 CPMAS spectrum of the complex of 1 with 2 moles of potassium phenoxide (7) is shown below. Here there is one instance of peak overlap in the 20-35 ppm region and another in the 68-82 ppm range but it is evident that there are ten unique carbon environments for the crown ether. In addition there are six clearly defined aromatic carbon resonances in the region of 110-175 ppm. This indicates that the structure of this complex is such that there must be a centre of symmetry or a plane of symmetry which bisects the macrocyclic cavity. Furthermore the appearance of six aromatic carbon resonances suggests that the two phenyl moieties are arranged in the crystal such that they are equivalent, but the magnetic environment of each of the six aromatic carbons is unique.

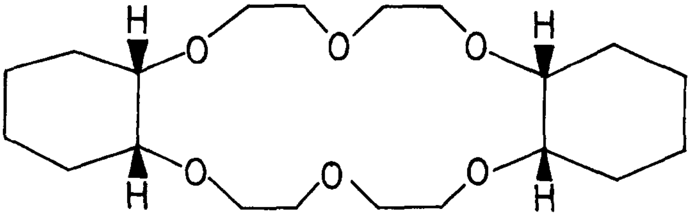


These conclusions are consistent with a recently completed x-ray study (8) on this novel structure in which a centre of symmetry for the complex has been observed. The potassium ions are out of the "pocket" of the macrocyclic ring and are complexed to only four of the macrocyclic oxygen atoms. The planes of the macrocycle and of the phenoxide ring are approximately parallel. The aromatic carbons C-2 and C-3 adjacent to the cyclohexyl group are found to be in different magnetic environments than their C-6 and C-5 counterparts respectively.

In the absence of x-ray data, an alternative explanation for the observed aromatic carbon non-equivalence in this complex could have been that the chemically equivalent (in solution) C-2,6 and C-3,5 sites are rendered magnetically non-equivalent in the solid by crystal packing forces. Such effects have been noted in the C-13 CPMAS spectrum of benzo-15-crown-5 itself (9).

Although complete assignments are not possible at present, it is evident that several phenoxide chemical shifts in the solid are substantially different from those found in solution. For this complex in methanol solution the C-13 resonances occur at 167.6, 119.7, 129.8, and 114.9 ppm for C-1; C-2,6; C-3,5; and C-4 respectively. In the solid spectrum, C-1 is noticably *deshielded* and appears near 175 ppm. By contrast, C-4 is *shielded* by *ca*. 4.5 ppm in the solid, since it resonates near 110 ppm in the CPMAS spectrum.

In methanol solution it is most likely that solvent-separated ion pairs exist for this complex while in the crystal it is found (8) that there is direct contact between the potassium ions and the phenoxide ions. As a result the electronic distribution at the phenoxide oxygen (and hence at the aromatic carbons) will differ in the solid from that present in solution. Accordingly chemical shift differences of this magnitude between solid and solution spectra are not unexpected for ionic materials. For the *cis-syn-cis* isomer (2) below, complexed with 2 moles of sodium phenoxide (7), the x-ray structure (8) indicates an irregular macrocyclic ring conformation in which no elements of symmetry exist.



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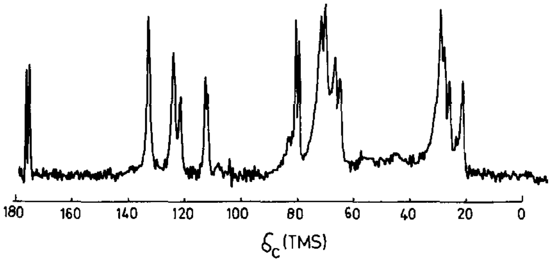
The C-13 CPMAS spectrum of this complex is shown below. Despite the instances of accidental resonance overlap it is clear that the elements of symmetry that were present for I and its potassium phenoxide complex are missing. For example, there are two resonances near 82 ppm, indicating that the cyclohexyl methine carbons bearing equatorial oxygens are now different. Furthermore, in the aromatic region, there are now two C-1 resonances near 175 ppm, and two C-4 lines near 112 ppm. This indicates that the two sodium phenoxide moities must be in different environments.



In conclusion, these results show that the C-13 CPMAS technique should be a valuable tool for the examination of the solid phase geometry of "host-guest" complexes, especially so in cases where x-ray data cannot be obtained. Detailed analysis of chemical shifts in the solid vs. those in solution should also lead to better overall understanding of factors contributing to C-13 shieldings.

References and Notes

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5. Spectra were obtained at 45.3 MHz on a Bruker CXP-180 NMR spectrometer, cross-polarization times of 2-5 ms were used, rf field amplitudes being 60 kHz. Normally 400 scans were sufficient. Sweep width was 20 kHz with 4 second recycle time. 2K data points were collected and fid's were zero filled to 8K before Fourier transformation. Magic angle spinning rates of ca. 3 kHz were achieved by using Kel-F spinners of the Andrew-Beams type.
6. In C-13 CPMAS spectra, the resonance intensities give reliable quantitative estimates provided that the carbons are of similar chemical type and are held in a rigid lattice (as is the case here). Sufficiently long cross polarization times must also be used. Care must be taken to ensure that there is no overlap of spinning sidebands in CPMAS spectra with "true" resonance positions.
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10. CPMAS is an acronym for Cross Polarization Magic Angle Spinning.

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