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High Resolution ^{13}C n.m.r. of Crystalline Benzo-15-crown-5 using Sideband Suppression Techniques

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Introduction

Since their initial discovery by Pedersen [1], the cyclic polyethers and their complexes have been extensively studied by X-ray crystallography. However, there is always uncertainty whether the same molecular structure exists in solution as in the solid state, especially if the crystal structure cannot be determined. Cross polarization magic angle spinning ^{13}C n.m.r. is a powerful method for the study of solids, but the high resolution spectra obtained can be complicated by features peculiar to the solid state. In order to understand the effect of crystal structure on the solid state spectra, it is necessary to study a series of compounds of known X-ray structure.

One such series, of considerable chemical interest, is that of benzo-15-crown-5 and its complexes with alkali and alkaline earth metal cations. In this preliminary communication we report the n.m.r. spectrum of solid benzo-15-crown-5 and demonstrate the considerable spectral simplification available by the use of the sideband suppression method developed by Dixon [2].

Experimental

The sample of benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin) used for the solid state n.m.r. spectrum was recrystallised from ethanol to give colourless crystals whose X-ray diffraction pattern was identical to that obtained from the crystal used in the X-ray crystal structure determination [3].

The cross polarization magic angle spinning spectra of the compound, shown in Fig. 1, were obtained using a Bruker CXP 300 n.m.r. spectrometer operated at 75 MHz for ^{13}C. The spectra were all acquired using a modest spinning rate of 3kHz, a frequency insufficient to eliminate all spinning sidebands (ssb) under conventional acquisition conditions (see Fig. 1a). However, when the new pulse sequence TOSS (Total Sideband Suppression) developed by Dixon is employed, almost complete suppression of sidebands is achieved. This results in a dramatic spectral simplification (Fig. 1b). Dixon's pulse sequence contains four ^{13}C π pulses subsequent to the contact pulse and prior to acquisition. For the spectra shown in Figs. 1b and 1c, this sequence was adapted to include phase alternation of π pulses, a 90° phase shift between the contact and π pulses, spin temperature inversion [4], quadrature phase routing and, where appropriate, (see Fig. 1c) suppression of non-quaternary carbon resonances [5].

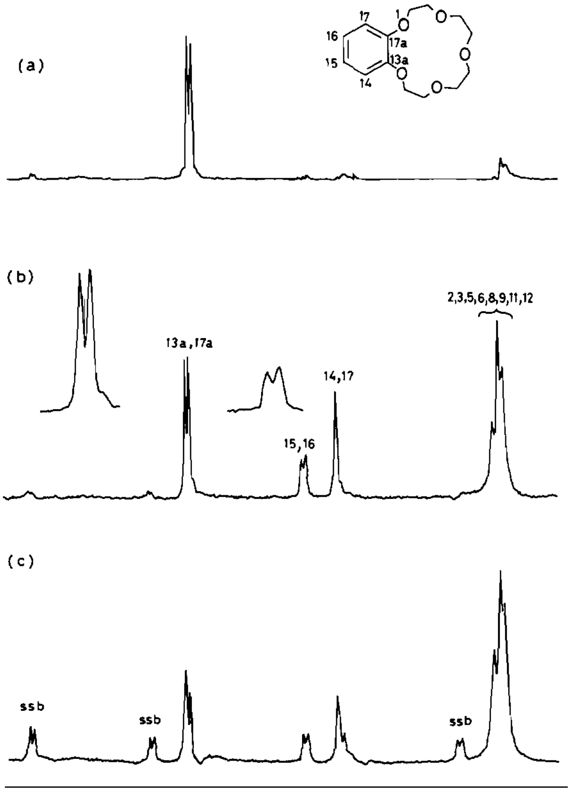

Fig. 1. CP MAS ^{13}C spectra of solid benzo-15-crown-5 with the following experimental conditions: (a) quadrature phase routing, spin temperature alternation, 5ms contact, 5s recovery period, 200 scans. (ssb = spinning side band). (b) As for (a) except pulse programme modified to include 4π pulses that comprise the Dixon TOSS sequence. (c) As for (b) except for a 45 μs window in the proton decoupling, included to bring about suppression of the non-quaternary ^{13}C signals.

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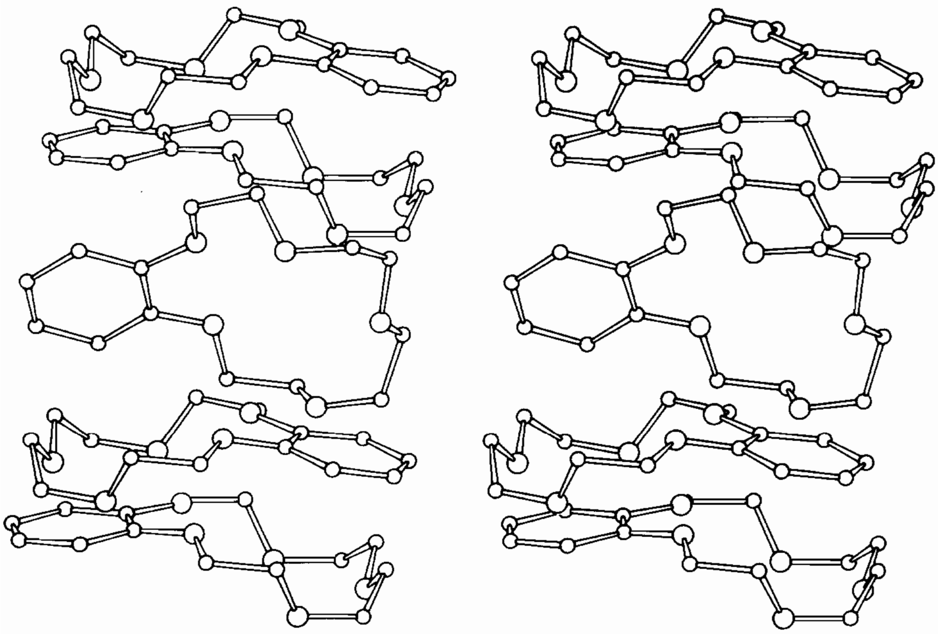

Fig. 2. Stereopair of five molecules of benzo-15-crown-5, as related in the crystal, taken from the co-ordinates in Reference 2.

Results and Discussion

Consideration of Fig. 1b shows that peaks centred at approximately 120 ppm and 150 ppm from TMS are split into symmetric doublets, with a splitting of approximately 1 ppm. However, in the solution state spectrum [6], these peaks are singlets. Further, the doublet at 148 ppm is the only signal with significant intensity under conditions of non-quaternary suppression (Fig. 1c) and may, therefore, be assigned to the quaternary carbon atoms labelled 13a and 17a. The remaining assignments of Fig. 1b have been made by direct comparison with the solution state spectrum, which shows three resonances for the aromatic carbon atoms.

The origin of the splittings of two of the aromatic peaks in the solid state spectrum can be understood by consideration of the X-ray crystal structure [3]. There is an approximate plane of symmetry within the benzo-15-crown-5 molecule, passing through the mid-points of the C_{15}–C_{16} and C_{13a}–C_{17a} bonds, and any small deviations in the heterocyclic ring are unlikely to explain the splittings in the aromatic ring carbons. However, the molecules of benzo-15-crown-5 pack such that the two sides of the benzene ring are inequivalent (Fig. 2). One side of each benzene ring points towards the benzene ring of a neighbouring molecule, whereas the other points towards a heterocyclic ring. The size of the splittings encountered here will depend on ring current effects and other intermolecular interactions. Preliminary calculations of ring current effects [7], indicate that these are insufficient to account for the observed splittings, suggesting that intermolecular interactions are important. We are continuing our investigations on a series of complexes of benzo-15-crown-5 of known and varied crystal structures in order to estimate these contributions and also those of anion contacts. A systematic study of this series should provide a useful insight into the effects of crystal packing and molecular conformation on the solid state ^{13}C high resolution n.m.r. spectra.

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