

A ^{13}C Cross Polarization–Magic Angle Spinning N.m.r. Study of the Structure of *p*-t-Butylcalix[4]arene–Toluene Clathrate in the Crystalline State

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^{13}C Cross polarization–magic angle spinning n.m.r. spectra of *p*-t-butylcalix[4]arene and *p*-t-butylcalix[4]arene–toluene clathrate in the solid state show that the ^{13}C chemical shift of the methyl carbon of toluene is displaced 6.2 p.p.m. upfield of that of free toluene which agrees well with the calculated value based on the ring current effect of the phenyl groups of the calixarene; the ^{13}C chemical shifts of other carbons were also assigned.

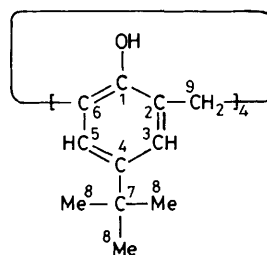
Recently, attention has been paid to a series of macrocyclic oligomers, the calixarenes.^{1†} The *X*-ray crystal structure of *p*-t-butylcalix[4]arene (1)–toluene clathrate was the first reported.² ^1H and ^{13}C N.m.r. spectra of calixarenes in solution have been reported with reference to transport phenomenon.³ No ^{13}C n.m.r. data have been previously reported for calixarene complexes in the solid state, which would give information about conformation in the crystalline state,⁴ relevant to the *X*-ray crystal structure.

Most interesting is to what extent the electronic structure, and therefore the ^{13}C n.m.r. chemical shift of a guest molecule, is affected by the spatial arrangement of the phenyl groups of the calixarene host molecule. Here we report a solid state ^{13}C n.m.r. study of the *p*-t-butylcalix[4]arene (1)–toluene complex of known *X*-ray crystal structure,² with special reference to the chemical shifts of carbon atoms of the guest molecule.

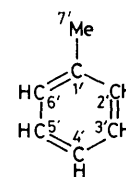
The ^{13}C cross polarization (c.p.)–magic angle spinning (m.a.s.) n.m.r. spectrum was recorded with a JEOL GX-270 Spectrometer (67.5 MHz) with a c.p.–m.a.s. accessory. The crystalline powder sample was contained in a bullet-type rotor and spun at 3–3.5 kHz. Contact time was 3 ms and repetition time 5 s. The ^{13}C chemical shifts were calibrated indirectly through external adamantane [methylene carbon of adamantane δ 29.5 relative to tetramethylsilane (TMS)]. The pulse

saturation transfer (p.s.t.)–m.a.s. ^{13}C spectrum was also recorded with a JEOL GX-270 Spectrometer.⁵ This method enhances the ^{13}C signal of mobile carbon atoms by the nuclear Overhauser effect (n.O.e.) with ^1H , while the c.p.–m.a.s. method does so for less mobile carbon atoms.

Figure 1 shows the ^{13}C c.p.–m.a.s. n.m.r. spectrum of the *p*-t-butylcalix[4]arene–toluene clathrate. Spinning side bands have been eliminated from the spectrum by the TOSS method. Based on the assignment of various calixarenes in solution,³ the signals at δ 146.64 and 144.60 were assigned to C(1) and C(4) of the *p*-t-butylcalix[4]arene, respectively. The peaks at δ 139.06 and 15.51 can be assigned to C(1') and C(7') carbons of the toluene included. The most intense peak, at δ 32.12 was assigned to C(8) of the calixarene.



p-t-Butylcalix[4]arene (1)



Toluene

† Cyclo{quater[(5-*t*-butyl-2-hydroxy-1,3-phenylene)methylene]}.

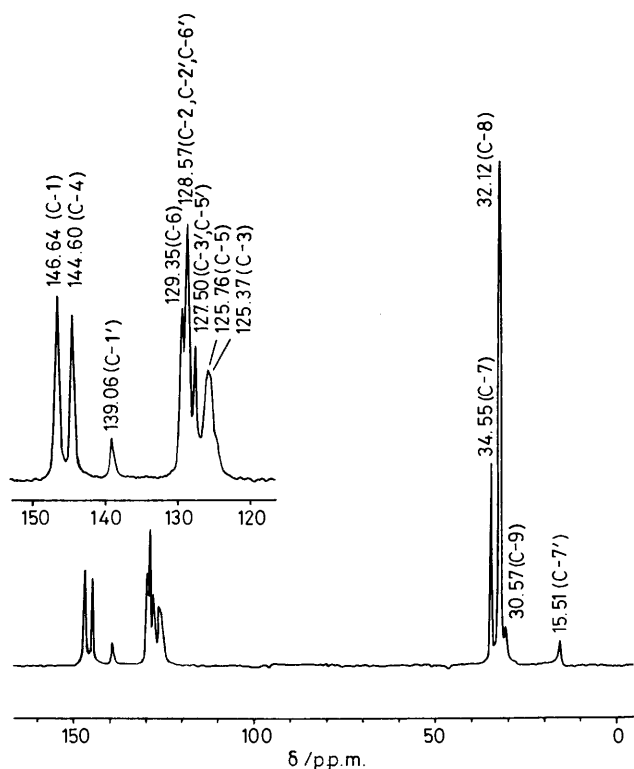


Figure 1. ^{13}C C.p.-m.a.s. n.m.r. spectrum of *p*-*t*-butylcalix[4]arene-toluene clathrate in crystalline state at room temperature.

Difficulty arose in the assignment of signals from C(2), C(3), C(5), C(6), C(7), and C(9) of the calixarene and C(2')—C(6') of toluene included in the cavity of the calixarene. A reference spectrum in solution is needed. No ^{13}C n.m.r. spectra are reported in the paper by Bocchi *et al.*,³ and it was difficult to measure the spectrum of *p*-*t*-butylcalix[4]arene in a solvent such as CDCl_3 because of its very low solubility. We, therefore, measured a ^{13}C n.m.r. spectrum of *p*-*t*-butylcalix[7]arene, highly soluble in CDCl_3 (the spectrum is not shown here). The assignment of signals to each carbon atom of the calix[7]arene was made by the gated decoupling method. Medium intensity signals at δ 147.7, 144.3, 127.3, and 126.0 were assigned to C(1), C(4), C(2) and C(3) of the calixarene, respectively. Signals at δ 34.0 (mw), 32.9 (w), and 31.5 (s) were assigned to C(7), C(9), and C(8), respectively. We also noted that the peak intensity for the bridge methylene carbon [C(9)] is very weak when compared with that for the Bu^t carbon [C(7)]. The chemical shifts of δ 34.55 (s), 32.12 (vs), and 30.57 (vw) for crystalline *p*-*t*-butylcalix[4]arene-toluene clathrate were thus assigned to C(7), C(8), and C(9) of the calixarene, respectively.

The ^{13}C p.s.t.-m.a.s. n.m.r. spectrum (Figure 2) shows two strong peaks at δ 128.67 and 127.50, assigned to C(2') and C(6'), and C(3') and C(5'), respectively, of the toluene guest. Comparison of the positions and intensities of these peaks in the two spectra (Figures 1 and 2) indicates that the strong peak at δ 128.57 may arise from both the C(2) or C(6) of the calix[4]arene and C(2') and C(6') carbons of the included toluene. Thus, the signals at δ 129.35 and 128.57 as shown in Figure 1 may be assigned to C(6) and C(2), respectively, or *vice versa*, and signals at δ 125.76 and 125.37 in Figure 1 to C(5) and C(3), respectively, or *vice versa*. The difference between the chemical shifts of the equivalent C(2) and C(6)

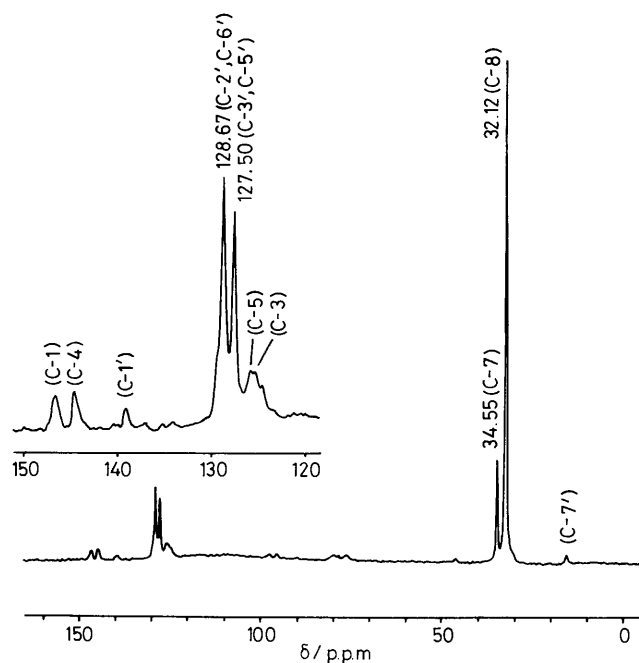


Figure 2. ^{13}C P.s.t.-m.a.s. n.m.r. spectrum of *p*-*t*-butylcalix[4]arene-toluene clathrate in crystalline state at room temperature.

carbons of the *p*-*t*-butylcalix[4]arene may be due to a particular arrangement of toluene in the cavity of the host molecule. This may also account for the chemical shift difference of C(3) and C(5).

The weak peak (at δ 15.51) assigned to methyl carbon C(7') of toluene in the clathrate, appeared 6.2 p.p.m. upfield relative to free toluene (at δ 21.3).⁶ The upfield shift is due to the ring current effect of the *p*-*t*-butylcalixarene. Using a relationship reported by Johnson *et al.*,⁷ that the theoretical chemical shift due to the ring current is given as a function of the position of a carbon atom measured from the centre of the benzene ring, the upfield shift of 6.2 p.p.m., a quarter (1.55 p.p.m.) of which, in the present case, arising from each phenyl ring of the *p*-*t*-butylcalix[4]arene, gives the position of the carbon atom in the cavity such that the methyl carbon of the toluene included is located 3.20 Å above the centre of each phenyl ring of the calixarene. This value was found to agree exactly with that measured from the crystallographic data for the *p*-*t*-butylcalix[4]arene-toluene clathrate.

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