

Direct synthesis of deep cavity *p*-phenylcalix[4]arene in PEG and its self association in the solid state

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Experimental Section

General Procedure: A mixture of *p*-phenylphenol and 37% aqueous formaldehyde solution were heated to 110°C under an inert atmosphere followed by addition of base (KOH, molar ratio 0.18). To the polymer formed, 20 ml of PEG 300 was added and the temperature raised to ca 220°C for one hour. On cooling to room temperature 100 ml of 1/1 1 M HCl/MeOH solution was added affording the calixarenes as a light brown solid which were collected and washed with water to remove any residual PEG. The mixture was then refluxed in MeOH and the products collected as a white solid, the ratio of the calixarenes present were identified using ¹H NMR spectroscopy.¹ Trituration with acetone afforded pure *p*-phenylcalix[4]arene. Isolation and NMR data for *p*-phenylcali[4,5,6,8]arenes have been reported earlier.² Similar outcome of this condensation reaction has also been achieved by using microwave energy under these conditions, 30 watts at 200 °C for a period of 10 minutes.

¹HNMR data:

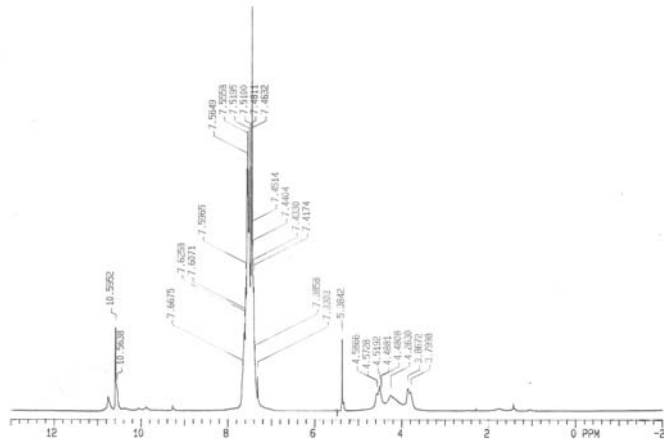
p-phenylcalix[6]arene: ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 4.05 (s-br, 12H; ArCH₂Ar), 7.22–7.49 (m, 42H; ArH), 10.57 (s, 6H; OH).

p-phenylcalix[5]arene: ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 4.01 (s-br, 10H; ArCH₂Ar), 7.25–7.49 (m, 35H; ArH), 9.11 (s, 5H; OH).

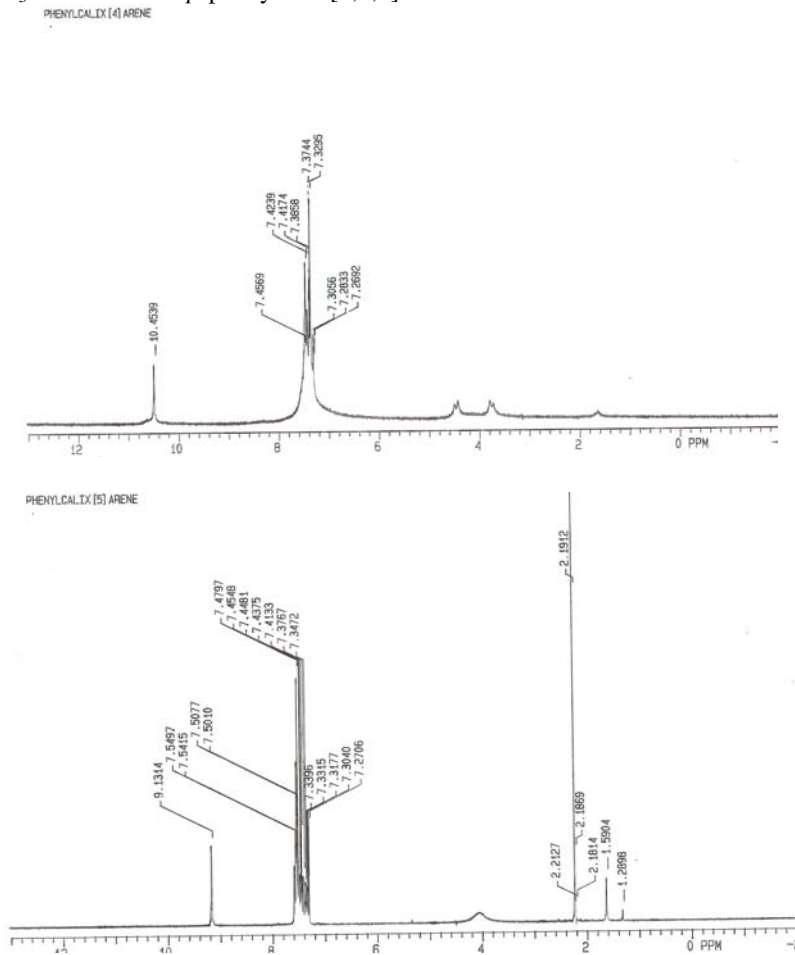
p-phenylcalix[4]arene: ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 3.67 (d, 4H; ArCH₂Ar; JAB=13.5 Hz), 4.38 (d, 4H; ArCH₂Ar; JAB=13.5 Hz) 7.20–7.49 (m, 28H; ArH), 10.43 (s, 4H; OH).

^1H NMR plots acquired on a 200 MHz Varian-Gemini spectrometer.

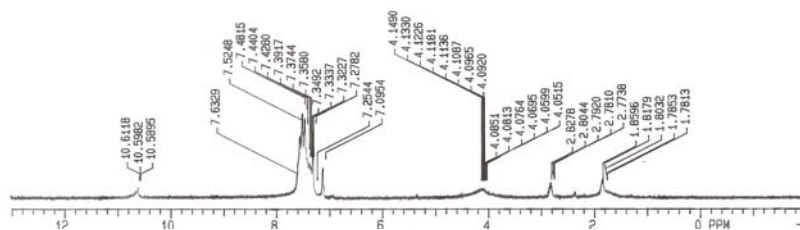
^1H NMR in CDCl_3 of the *p*-phenylcalix[4,5,6]arenes mixture upon precipitation from PEG



^1H NMR in CDCl_3 of the isolated *p*-phenylcalix[4,5,6]arenes via acetone trituration



PHENYLCALIX [6] ARENE



References:

1. M. Makha, C. L. Raston, B. W. Skelton, *Green Chem.*, 2004, **6**, 158.
2. M. Makha, C. L. Raston, *Tet. Lett.*, 2001, **42**, 6215.