Supplementary Material (ESI) for Chemical Communications

Concomitant formation of two different solvates of a hexa-host from a binary mixture of solvents

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Supplementary Material (ESI)

(7 pages)

Synthesis of 1

Hexafluorobenzene, 4-cyanophenol and DMSO were purchased from Aldrich Chemical Co. and used without further purification. Anhydrous potassium carbonate was obtained from SaarChem Pty. Ltd, RSA.

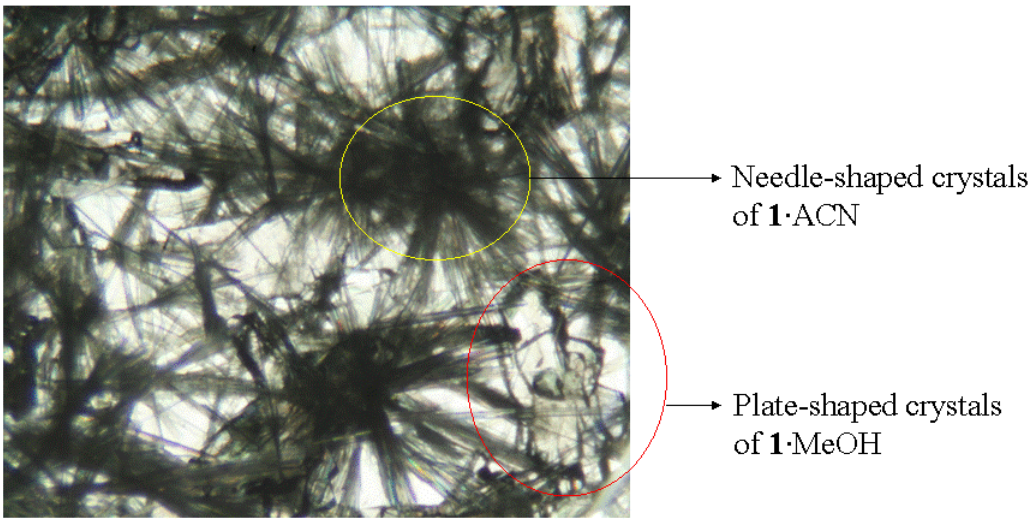
Hexafluorobenzene (10 mmol), 4-cyanophenol (70 mmol), and anhydrous potassium carbonate (140 mmol) were mixed in 50 mL DMSO. The mixture was first heated for 1 minute and then refluxed for 10 minutes in a microwave oven at 340 W. After cooling to room temperature, the resulting mixture was poured into ice-water to precipitate products and the solution was stirred for 10 minutes. The white product was filtered and dried in vacuo, and then washed with ethyl acetate. Recrystallization from dichloromethane yielded pure compound **1** which was characterized by ^{1}H and ^{13}C NMR after drying overnight in vacuo.

NMR data: ^{1}H (DMSO-d_6): δ7.11 (d, 12H), δ7.69 (d, 12H).

^{13}C (DMSO-d_6): δ159.69, δ138.94, δ134.74, δ118.91, δ116.92, δ106.38.

Preparation of 1·MeOH and 1·ACN:

Compound **1** was dissolved in an equal-volume mixture of MeOH and ACN which was allowed to evaporate slowly at room temperature. After four days, crystals with two different morphologies were observed.



Single-crystal X-ray diffraction:

Single crystal X-ray data were collected on Bruker SMART Apex diffractometer equipped with a CCD area detector.

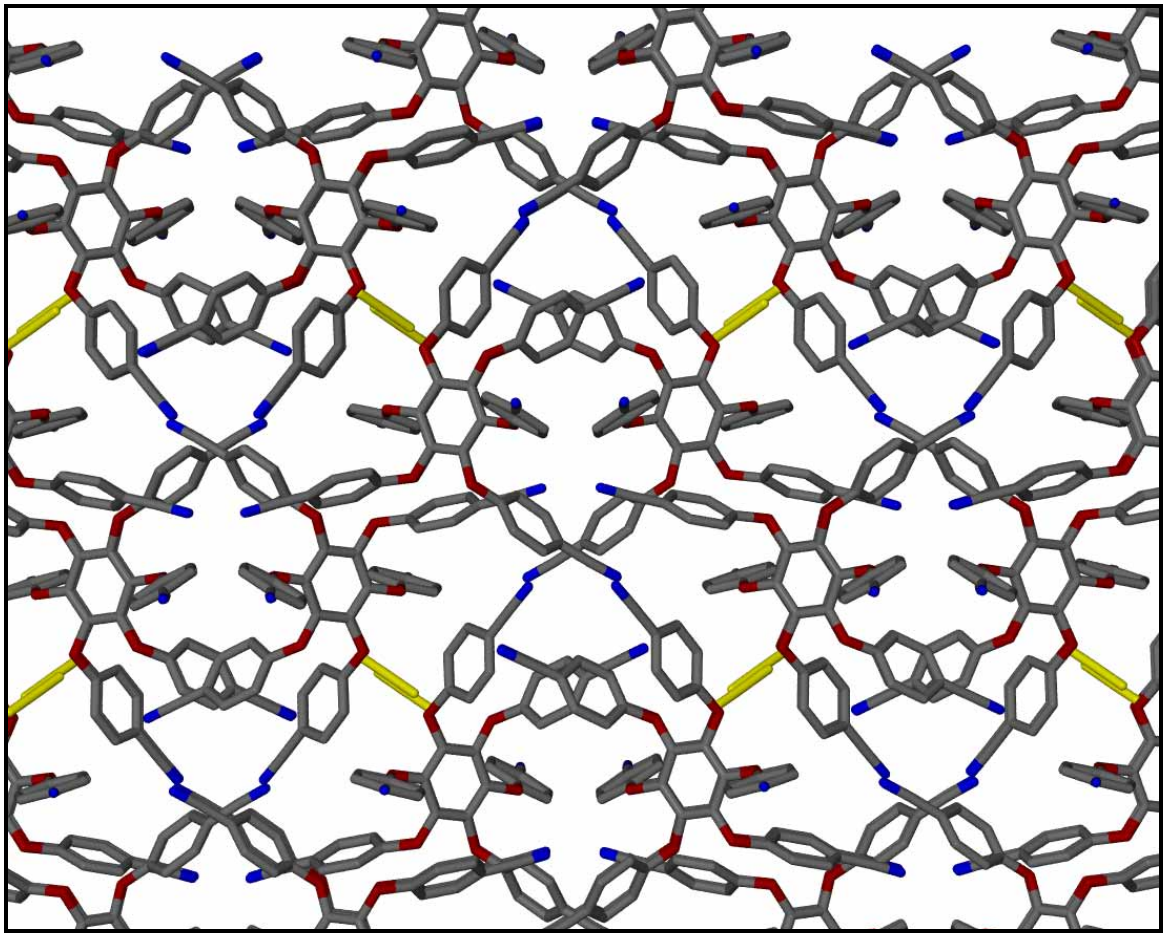


Fig 1. Packing diagram of **1**·ACN, viewed along the *b* axis. Hydrogen atoms are omitted for clarity. Acetonitrile molecules are shown in yellow.

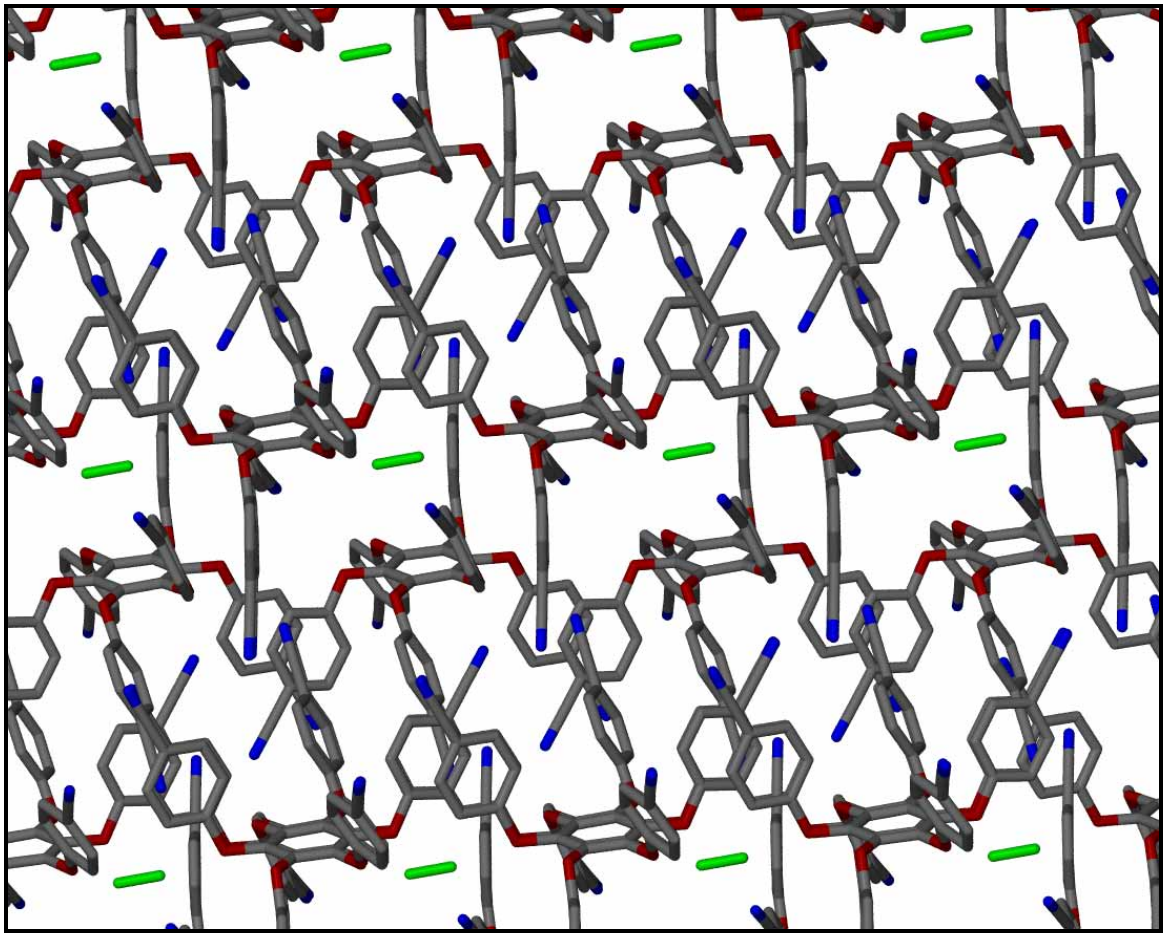


Fig 2. Packing diagram of **1**·MeOH viewed along the *c* axis. Hydrogen atoms are omitted for clarity. Methanol molecules are shown in green.

NMR spectroscopy:

All the NMR spectra were recorded on a Varian VNMRS 400 MHz Spectrometer. Samples were dissolved in deuterated DMSO.

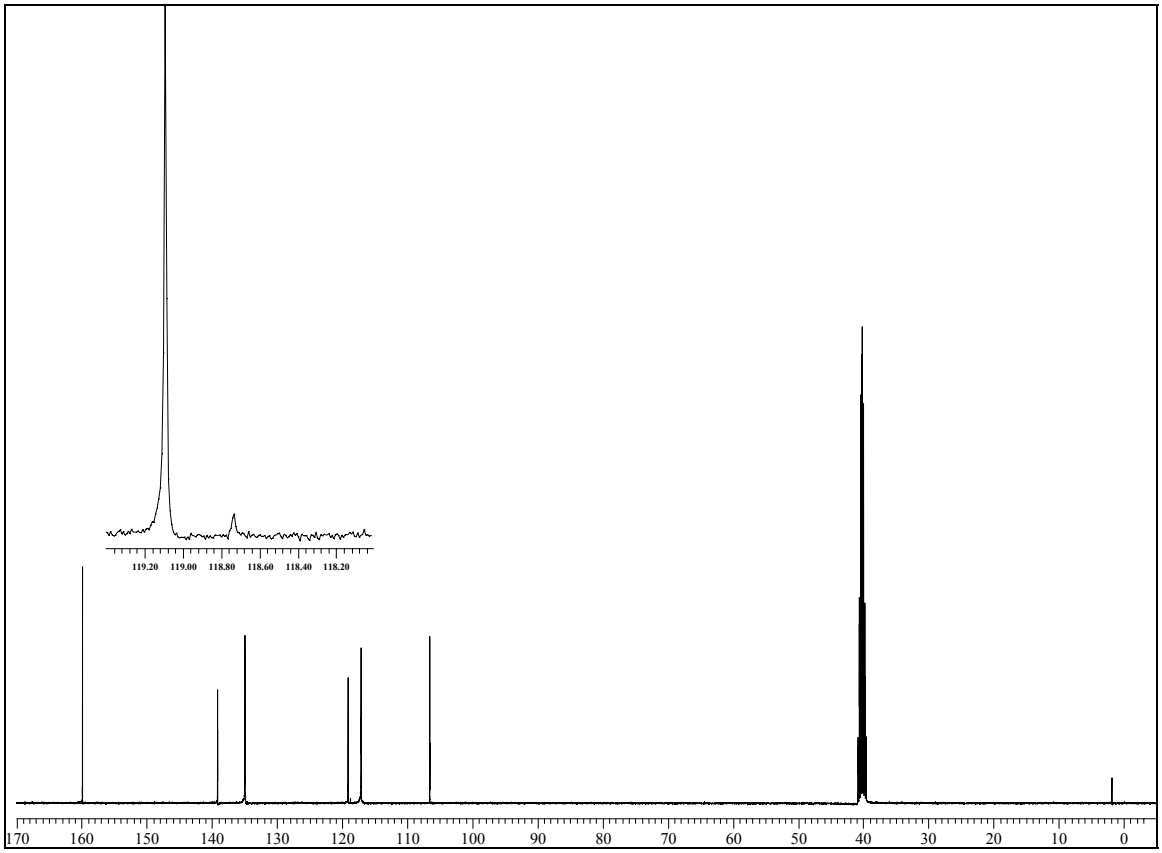


Fig 3. ^{13}C NMR Spectrum of **1**·ACN. The methyl carbon of acetonitrile produces a peak at 1.87 ppm and the cyano carbon of acetonitrile is observed at 118.73 ppm (inset).

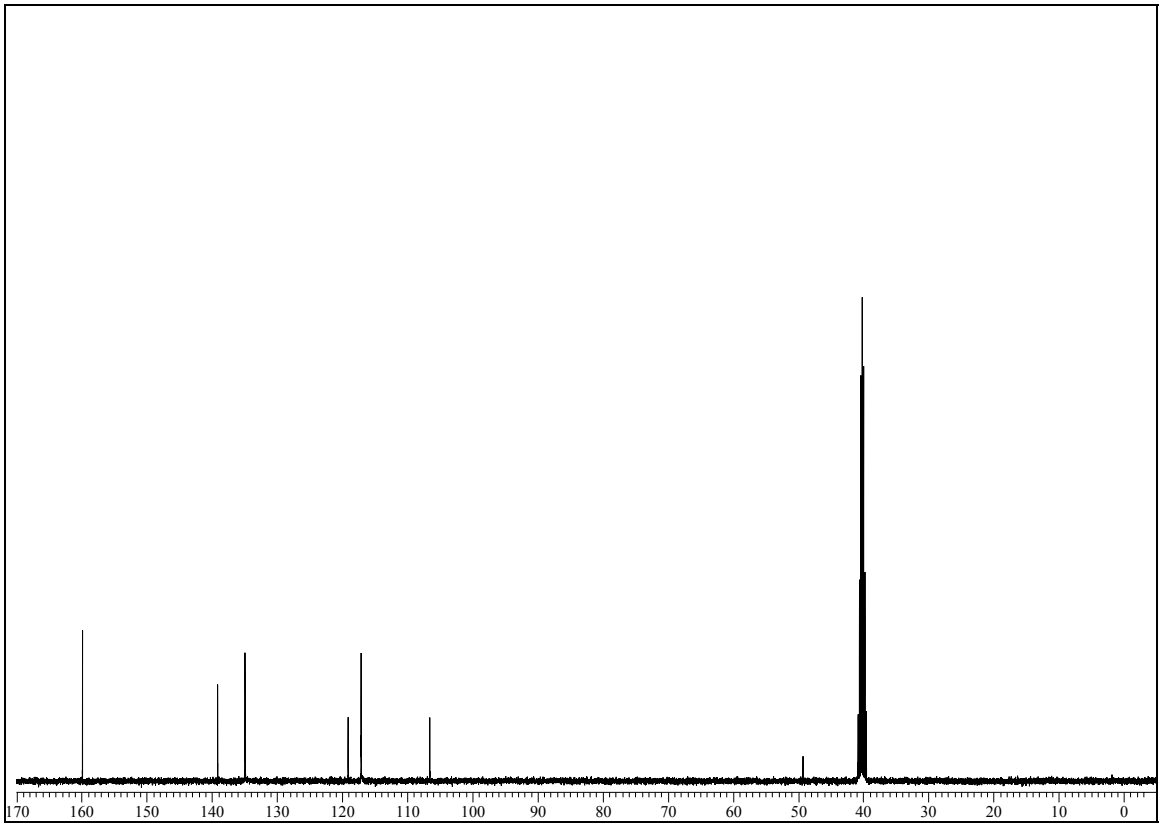


Fig 4. ^{13}C NMR Spectrum of **1**·MeOH. The methyl carbon of methanol is observed at 49.3 ppm.

Table 1. Hydrogen bonding geometry in **1**·MeOH and **1**·ACN*

	D–H…A	D–H (Å)	H…A (Å)	D…A (Å)	∠D–H…A (°)
	O(7)–H(7)…N(1)	0.98	2.02	2.969(3)	162
	C(8)–H(8)…N(3)	1.08	2.56	3.306(3)	125
	C(19)–H(19)…N(5)	1.08	2.43	3.398(3)	148
	C(22)–H(22)…N(6)	1.08	2.47	3.454(3)	150
	C(26)–H(26)…N(5)	1.08	2.52	3.303(3)	128
1·MeOH	C(29)–H(29)…O(7)	1.08	2.40	3.343(3)	144
	C(30)–H(30)…N(1)	1.08	2.56	3.548(3)	151
	C(39)–H(39)…N(4)	1.08	2.49	3.501(3)	155
	C(43)–H(43)…O(7)	1.08	2.28	3.291(3)	155
	C(46)–H(46)…N(2)	1.08	2.39	3.390(3)	153
	C(49)–H(49A)…O(1)	1.08	2.45	3.534(3)	174
	C(8)–H(8)…N(1)	1.08	2.61	3.648(7)	161
	C(12)–H(12)…N(6)	1.08	2.50	3.341(6)	133
	C(15)–H(15)…O(2)	1.08	2.54	3.149(5)	115
	C(15)–H(15)…O(3)	1.08	2.42	3.171(5)	125
1·ACN	C(19)–H(19)…N(6)	1.08	2.54	3.384(6)	134
	C(23)–H(23)…N(1)	1.08	2.55	3.328(7)	128
	C(29)–H(29)…N(3)	1.08	2.41	3.217(7)	130
	C(39)–H(39)…N(4)	1.08	2.36	3.265(6)	140
	C(44)–H(44)…N(7)	1.08	2.33	3.399(7)	171
	C(47)–H(47)…N(4)	1.08	2.51	3.563(6)	165

*All hydrogen atoms were placed in calculated positions with C-H and O-H bond distances neutron-normalized.