Supplementary Material (ESI) for Chemical Communications

Stable supramolecular dimer of self-complementary benzo-18-crown-6 with pendant protonated amino arm

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General

Chemicals (reagent grade) and solvents were purchased from Aldrich or Acros and used as received. NMR spectra were recorded on a Bruker AM-300 spectrometer, mass-spectra (electrospray ionization) were measured at Mass Consortium (San Diego, CA).

Procedures

Benzo-18-crown-6 was prepared from dichloropentaethylene glycol and catechol according to procedure for benzo-15-crown -5 analog adapted from Wu and co-workers . *[Y.Wu, H.An, J.Tao, J.S.Bradshaw, R.M.Izatt Journal of Inclusion Phenomena, 1990, 9, 267-274]* in 60% yield.

4'-Formylbenzo-[18-crown-6] was obtained form benzo-18-crown-6 accordingly to the published procedure *[E.M.Hyde, B.L.Shaw, I.Shepherd, J.C.S.Dalton, 1696-1705]* with work up adopted from Shuying *[T. Shuying, W. Yuting, P.Changhong, Huaxue Shiji, 2000, 22(1), 49-51]*. Yield: 55%

(4')-Hydroxymethylbenzo-[18-crown-6]

4'-Formylbenzo-18-crown-6 (3.2 g, 9.4 mmol)) was suspended in 30 ml of absolute ethanol, and the mixture was cooled to 0°C. Sodium borohydride (0.34 g, 9.0 mmol) was added to this suspension in small portions, maintaining the temperature below 7°C. After the addition of sodium borohydride, the mixture was stirred at 0°C for 1 hr 40 min, and then the solvent was rotary evaporated. The residue was washed with water and extracted with methylene chloride (3x30 ml). The combined extracts were dried over magnesium sulfate, filtered, and rotary evaporated, yielding 2.7 g (7.9 mmol, 84 %). of an oily product. ^{1}H NMR ($CHCl_3$-d): δ 6.95 (d, J= 1.7 Hz, 1H), 6.89 (dd, J = 8.1, 1.7 Hz, 1H),

6.82 (d, J=8.1, 1H), 4.62 (s, 2H), 4.20 -4.13 (m, 4H), 4.00 - 3.95 (m, 4H), 3.8 - 3.76 (m, 4H), 3.72 - 3.70 (m, 4H), 3.68 (s, 4H), 2.66 (br.s. 1H). Anal. Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65; found: C, 58.69; H, 7.77. M/z (ESMS): 341 ($[M-H]^-$), 343 ($[MH]^+$).

(4')-Chloromethylbenzo-[18-crown-6] 4-Hydroxymethylbenzo-18-crown-6 (2.7 g, 7.9 mmol) was dissolved in 170 ml of methylene chloride and fine powder of potassium carbonate (3.60 g, 26.1 mmol)was added. The mixture was colled down to 0^0 C under N_2, and thionile chloride (2.07 g, 17.38 mmol) was added. The reaction was stirred for 45 min, then filtered, and the solvent was removed on a rotary evaporator, yielding 2.55 g (7.07 mmol, 90 %) the of material. ^{1}H NMR ($CHCl_3$-d): δ 6.91 (m, 2H), 6.80 (d, J = 8.0, 1H), 4.61 (s, 2H), 4.23 - 4.15 (m, 4H), 4.00 - 3.92 (m, 4H); 3.79 - 3.75 (m, 4H); 3.73 - 3.68 (m, 12H). ^{13}C NMR ($CHCl_3$-d): δ 148.8, 144.5, 130.7, 121.8, 115.1, 113.3, 70.9, 70.8, 69.5, 68.9, 63.5, 46.7. M/z (ESMS): 361 ($[MH]^+$), 399 ($[M+K]^+$).

Phtalimidomethylbenzo-[18-crown-6] Chloromethylbenzo-18-crown-6, (2.55 g, 7.07 mmol) and potassium phtalimid (1.39 g, 7.50 mmol) were mixed with 24 ml of dimethylformamide and heated at 90^0 C for 1 hr. The reaction mixture was cooled, 60 ml of chloroform were added, and the mixture was poured into 250 ml of water. The chloroform layer was separated, and the aqueous layer was extracted with an additional amount of chloroform (2x200 ml). The combined chloroform extracts were washed with 0.15 M NaOH (2x300 ml), and with water (4x400 ml). The chloroform extract was dried over magnesium sulfate, filtered, and rotary evaporated, yielding 2.8 g of an oily product, which was recrystallized from ethanol. Yield: 2.2g (4.67 mmol, 66%). ^{1}H NMR ($CHCl_3$-d): δ 7.86- 7.83 (m, 2H), 7.73 - 7.70 (m, 2H), 7.00 - 6.97 (m, 2H), 6.80 (d, J = 8.7, 1H), 4.74 (s, 2H), 4.13-4.10 (m, 2H), 4.09-4.06 (m, 2H), 3.89 - 3.84 (m, 4H), 3.72 (s, 8H). ^{13}C NMR ($CHCl_3$-d): δ 168.5, 149.4, 134.4, 132.6, 130.0, 123.7, 122.3, 115.3, 114.6, 71.3, 71.2, 70.0, 69.6, 41.8.). Anal. Calcd for $C_{25}H_{29}NO_6$: C, 63.68, H, 6.20, N 2.97; found: C, 63.70, H, 6.07, N 2.66. M/z (ESMS): 472 ($[MH]^+$), 494 $[M+Na]^+$.

*(4')-Aminomethylbenzo-[18-crown-6]**(1)*** The phthalimide derivative of 4-methylbenzo-18-crown-6 (1.9 g, 4.0 mmol) was dissolved in 50 ml of hot ethanol. To this solution0.513g (16.0 mmol) of anhydrous hydrazine in 18 ml of ethanol was added, and the reaction mixture was refluxed for 2 hrs. The reaction mixture was cooled on an ice bath and filtered, the precipitate of phtalhydrazide was washed with ice-cold ethanol. The combined

filtrates were rotary evaporated, producing 1.2 g of crude off-white semi-crystalline solid. The residue was washed with chloroform; and undissolved solid residue was discarded. The chloroform filtrate was rotary evaporated to a final volume of about 20 ml, and refrigerated for several hours. An additional amount of solid phthalhydrazide formed was separated by filtration, and the solvent was removed by rotary evaporation. The residue was treated with 20 ml of hot acetonitrile and filtered. Evaporation of the solvent resulted in transparent yellow oil of the product. Yield: 1.19g (3.49mmol, 87%)

^{1}H NMR (CH_3Cl-d_3): δ 1.98 (br.s, 2H); 3.65 (s, 4H); 3.70- 3.75 (m, 8H), 3.77 (s, 2H); 3.87-3.90 (m, 4H); 4.10-415 (m, 4H); 6.80 (s, 1H); 6.87 (d, J 9Hz,2H).

^{13}C NMR ($CHCl_3$-d): 149.1; 148.0; 135.3 120.5; 114.4; 113.7; 71.15; 71.11; 71.05; 71.01; 70.0; 69.4, 69.3; 46.1.

Electrospray: $[M-H]^-$ 340, $[MH]^+$ 342 (MW = 341.4).

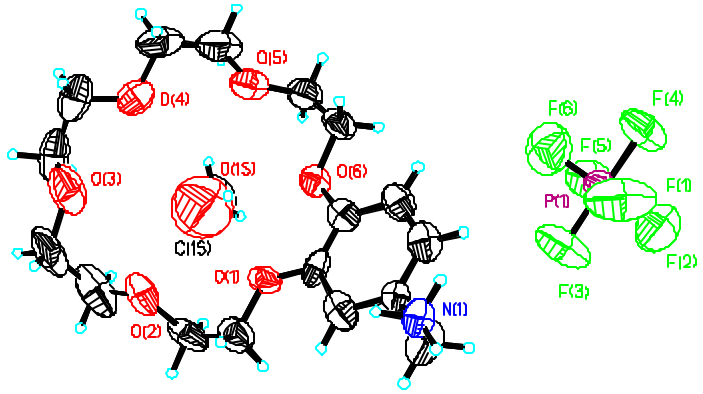
X-ray data

X-ray data were collected using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[1] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[2] which corrects for Lp and decay. Absorption corrections were applied using SADABS[6] supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97[3] program and refined by least squares method on F^2, SHELXL-97, [4] incorporated in SHELXTL-PC V 5.10.[5]

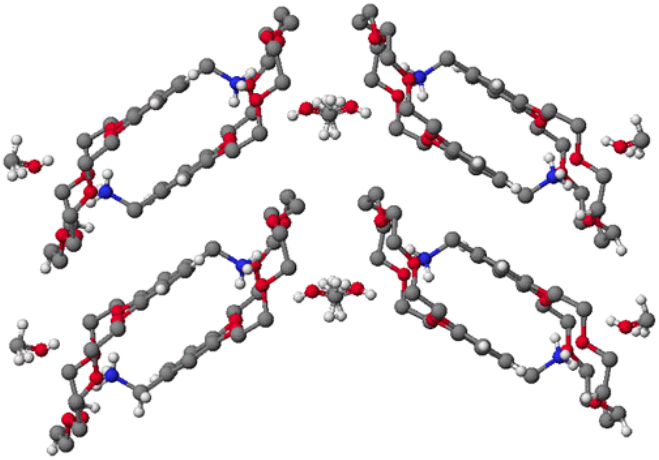
The structure was solved in the space group C 2/c (# 15) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. A methanol solvate was found to be disordered in the crystal lattice. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsoids.

1. SMART V 5.050 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (1998).
2. SAINT V 5.01 (NT) *Software for the CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (1998).
3. Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990.
4. Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.
5. SHELXTL 5.10 (PC-Version), *Program library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems, Madison, WI (1998).
6. SADABS. *Program for absorption corrections using Siemens CCD based on the method of Robert Blessing*; Blessing, R.H. Acta Cryst. A51 (1995) 33-38.

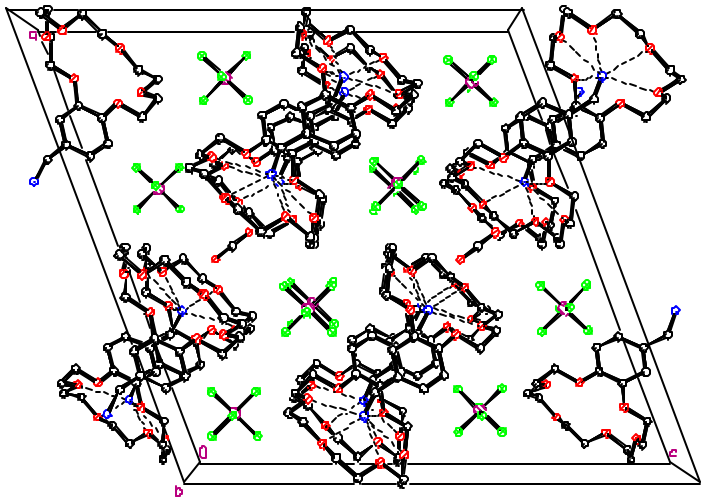
X-ray structure of **1-HPF$_6$·0.5MeOH**



(A) single molecule



(B) Packing



(C) Unit cell

^{1}H NMR spectra

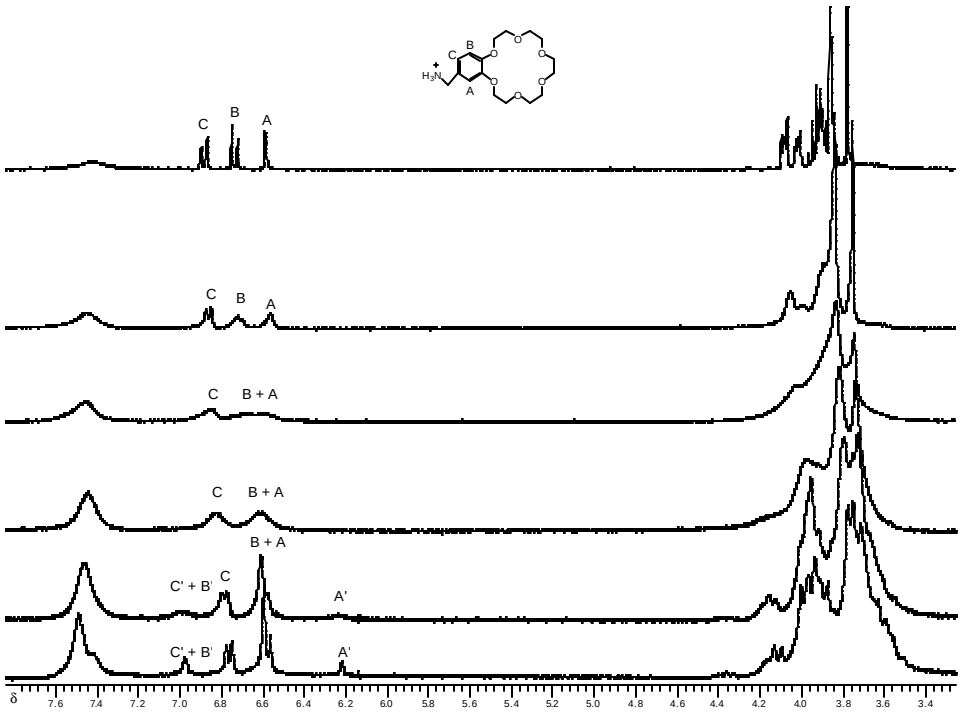


Figure 1. Temperature dependent ^{1}H NMR spectra of **1-HPF$_6$** (10^{-2} M) in CD_3CN; from top to bottom: 243 K, 313 K, 295 K, 283 K, 273 K, 238 K.

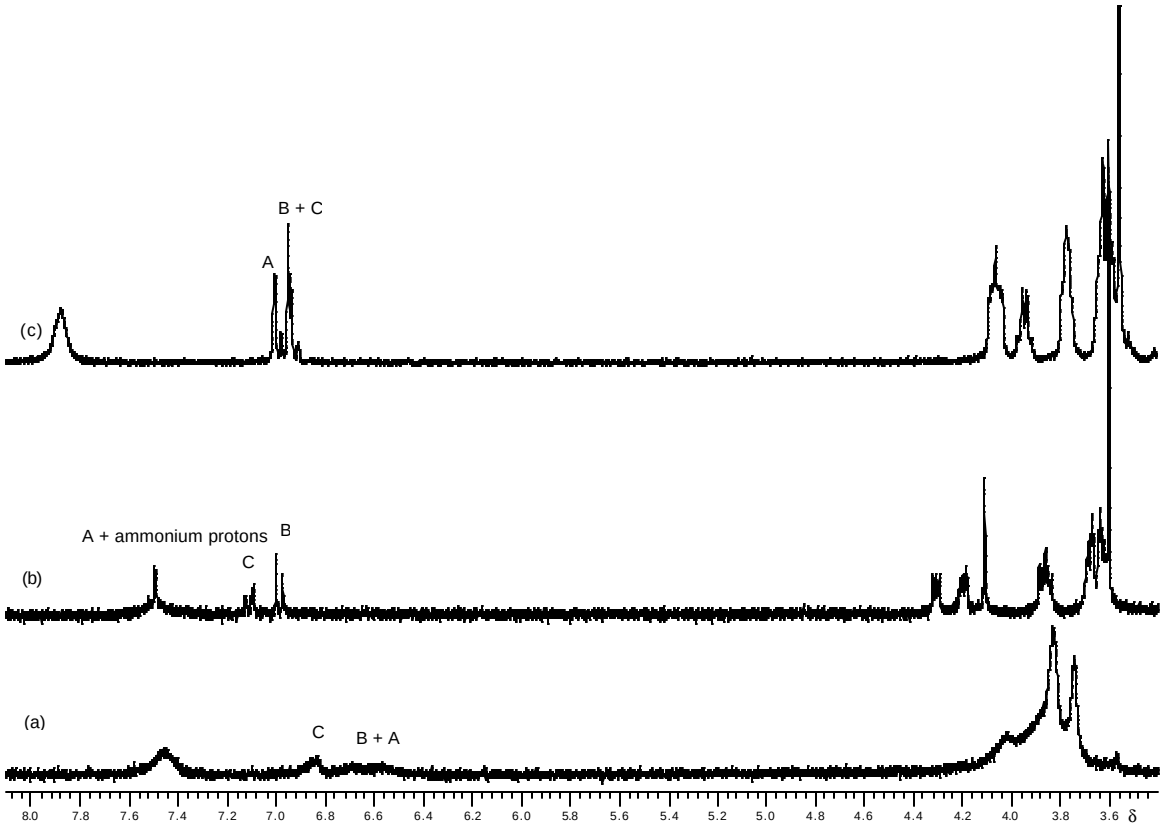


Figure 2. ^{1}H NMR spectra at 295 K: (a) the dilute solution of **1**-HPF_6 (10^{-4} M) in CD_3CN; (b) the dilute solution of **1**-HPF_6 (10^{-4} M) in CD_3CN upon the addition of excess KI; (c) solution of **1**-HPF_6 (10^{-2} M) in DMSO.