Experimental Section

1: *t*BuSSiMe$_3$ (0.53 mL, 2.7 mmol) was added to a suspension of [Fe(CO)$_4$(HgCl)$_2$] (0.43 g, 0.67 mmol) in toluene (20 mL) at room temperature. A yellow powder precipitated immediately, and the solution turned yellow within two days. After three days orange needles of **1** were formed in the solution (yield 45 %).

2: *t*BuSSiMe$_3$ (0.18 mL, 0.9 mmol) was added to a suspension of [Fe(CO)$_4$(HgBr)$_2$] (0.34 g, 0.47 mmol) in toluene (20 mL) at room temperature. The brown solution was layered with *n*-heptane and after two weeks small orange crystals of **2** were formed together with a black-brown precipitate (yield 15 %).

3 *t*BuSSiMe$_3$ (0.27 mL, 1.4 mmol) was added to a suspension of [Fe(CO)$_4$(HgBr)$_2$] (0.50 g, 0.7 mmol) in toluene (20 mL) at room temperature. Within a few weeks, a light brown precipitate and orange crystals of **3** were formed from the yellow-brown solution (yield 30 %). Satisfactory elemental analyses (Hg, Fe, C, and H) were obtained for **1**–**3**.

Received: November 27, 1997 [Z 11205 IE]
German version: *Angew. Chem.* **1998**, *110*, 1288–1291

Keywords: clusters · iron · mercury · S ligands · structure elucidation

---

[1] I. Dance, K. Fischer, *Prog. Inorg. Chem.* **1994**, *41*, 637.

[2] H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, *105*, 1364; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1303.

[3] J. F. Corrigan, D. Fenske, *Chem. Commun.* **1996**, 943; J. F. Corrigan, D. Fenske, W. P. Power, *Angew. Chem.* **1997**, *109*, 1224; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1176.

[4] S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde, U. Woggon, *Angew. Chem.* **1996**, *108*, 2360; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2215.

[5] N. Herron, J. C. Calabrese, W. E. Farneth, Y. Wang, *Science* **1993**, *259*, 1426; T. Vossmeier, G. Reck, B.Schulz, L. Katsikas, H. Weller, *J. Am. Chem. Soc.* **1995**, *117*, 12881.

[6] H. Hock, H. Stuhlmann, *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2097; *Ber. Dtsch. Chem. Ges. B* **1929**, *62*, 431.

[7] R. Ahlrichs, M. von Arnim, J. Eisenmann, D. Fenske, *Angew. Chem.* **1997**, *109*, 243; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 233.

[8] J. J. Vittal, P. A. W. Dean, N. C. Payne, *Can. J. Chem.* **1993**, *71*, 2043; P. A. W. Dean, J. J. Vittal, Y. Wu, *Inorg. Chem.* **1994**, *33*, 2180.

[9] A. J. Canty, C. L. Raston, A. H. White, *Aust. J. Chem.* **1978**, *31*, 677.

[10] T. Alsina, W. Clegg, K. A. Fraser, J. Sola, *J. Chem. Soc. Chem. Commun.* **1992**, 1010.

[11] X-ray structure analysis: Stoe-IPDS (Mo$_{K\alpha}$ radiation); data collection and refinement (SHELXS-86, SHELXL-93).
1: monoclinc, space group $P2_1/n$ (no. 14), $Z=4$, $T=200$ K, $a=1106.4(2)$, $b=4379.6(9)$, $c=1208.7(2)$ pm, $\beta=107.69(3)^\circ$, $V=5580(2)\times10^6$ pm^3, $\mu(\mathrm{Mo_{K\alpha}})=206.57$ cm^{-1}, $2\Theta_{max}=48^\circ$, 17550 reflections (empirical absorption correction), 7529 independent reflections ($R_{int}=0.1259$) and 6014 observed with $I>2\sigma(I)$, 622 parameters (Hg, Fe, Cl, S, O, and C anisotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 3.868 e Å^{-3}, $R1=0.0758$, $wR2=0.2407$. $\mathbf{2}\cdot2\,C_7H_8$: monoclinic, space group $C2/c$ (no. 15), $Z=4$, $T=200$ K, $a=3061.7(8)$, $b=1651.2(6)$, $c=3244.9(10)$ pm, $\beta=110.97(2)^\circ$, $V=15318(8)\times10^6$ pm^3, $\mu(\mathrm{Mo_{K\alpha}})=205.43$ cm^{-1}, $2\Theta_{max}=45^\circ$, 36397 reflections (empirical absorption correction), 9740 independent reflections ($R_{int}=0.0874$) and 6748 observed with $I>2\sigma(I)$, 695 parameters (Hg, Fe, Br, S, O, and C anisotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 2.394 e Å^{-3}, $R1=0.0501$, $wR2=0.1333$. With the disordered Hg7 atom an occupation of 1/3 was assumed for the threefold disordered position. $\mathbf{3}\cdot5\,C_7H_8$: monoclinic, space group $I2/a$ (no. 15), $Z=4$, $T=190$ K, $a=3145.9(6)$, $b=3205.8(6)$, $c=3380.2(7)$ pm, $\beta=101.62(3)^\circ$, $V=33391(12)\times10^6$ pm^3, $\mu(\mathrm{Mo_{K\alpha}})=224.80$ cm^{-1}, $2\Theta_{max}=45^\circ$, 59953 reflections (empirical absorption correction), 21145 independent reflections ($R_{int}=0.1009$) and 14405 observed with $I>2\sigma(I)$, 1099 parameters (Hg, Br, Fe, and S anisotropic; O and C isotropic; the positions of the H atoms were calculated for ideal positions), max. residual electron density: 2.775 e Å^{-3}, $R1=0.0628$, $wR2=0.1718$. The heavy-metal skeleton of **3** is partly disordered (Hg12–Hg15, Fe7, Fe11, Br6, Br7, Br11, and S9). An indication of a possible superstructure could not be found. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), (fax: (+49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-408008, CSD-408009, and CSD-408010.

[12] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192.

[13] C. L. Raston, A. H. White, S. B. Wild, *Aust. J. Chem.* **1976**, *29*, 1905.

[14] W. Gäde, E. Weiss, *Angew. Chem.* **1981**, *93*, 796; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 803.

[15] K. Brodersen, A. Knörr, *Z. Naturforsch. B* **1990**, *45*, 1193.

[16] K. Brodersen, G. Liehr, W. Rölz, *Z. Anorg. Allg. Chem.* **1977**, *428*, 166.

[17] For the estimation of the valence sum according to Brese and O'Keeffe,[12] the bonding-valence parameters were taken from their publication. A value of 2.47 was assumed for Hg–Fe(CO)$_4$ (not given in ref. [12]).

[18] M. A. Witener, J. K. Baschkin, K. S. Hagen, J.-J. Girerd, E. Gamp, N. Edelstein, R. H. Holm, *J. Am. Chem Soc.* **1986**, *108*, 5607.

Supramolecular Daisy Chains**

Peter R. Ashton, Ian Baxter, Stuart J. Cantrill,
Matthew C. T. Fyfe, Peter T. Glink, J. Fraser Stoddart,*
Andrew J. P. White, and David J. Williams*

The appeal that interlocked molecular assemblies and intertwined superarchitectures holds for chemists is reflected in the extensive literature[1] devoted to the construction and characterization of such systems. A natural development is the fabrication of interwoven[2] supermolecules and supramolecular arrays by the noncovalent oligomerization/polymerization[3] of self-complementary (plerotopic[4]) monomeric species. An approach that offers much potential involves[5] a plerotopic macrocyclic monomer that can oligomerize or polymerize through noncovalent bonds. However, this monomer must be designed in such a way that its two complementary sites are compelled to recognize each other in an intermolecular,[6] rather than an intramolecular,[7] sense; that is, the plerotopic monomer must be prevented from "biting its own tail" and encouraged to form a "daisy chain"[8] instead (Figure 1).

---

[*] Prof. J. F. Stoddart,[+] P. R. Ashton, S. J. Cantrill, Dr. M. C. T. Fyfe, Dr. P. T. Glink
School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT (UK)
Prof. D. J. Williams, Dr. I. Baxter, Dr. A. J. P. White
Chemical Crystallography Laboratory
Department of Chemistry, Imperial College
South Kensington, London SW7 2AY (UK)
Fax: (+44) 171-594-5835

[+] Current address:
Department of Chemistry and Biochemistry
University of California, Los Angeles, CA 90095 (USA)
Fax: (+1) 310-206-1843
E-mail: stoddart@chem.ucla.edu

[**] This research was sponsored in the UK by the Engineering and Physical Sciences Research Council.

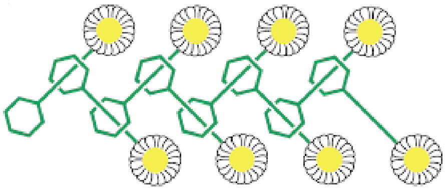
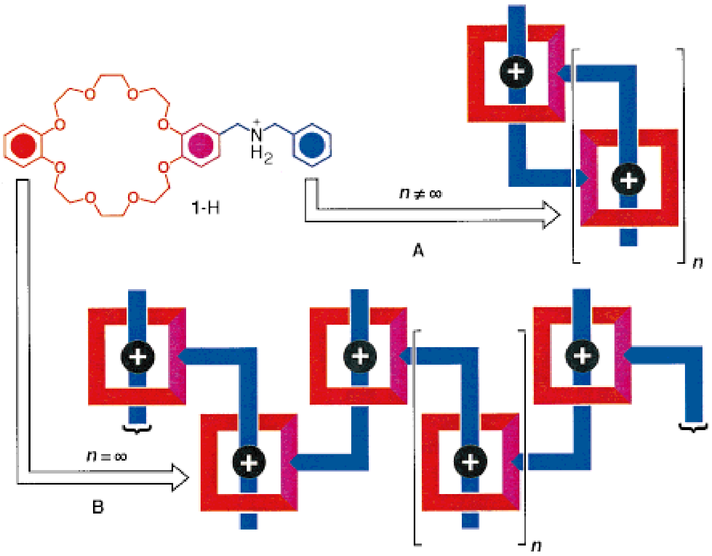


Figure 1. Cartoon representation of a supramolecular daisy chain.

When this hurdle has been surmounted, another issue has to be addressed: Will the self-complementary monomer oligomerize noncovalently to form a discrete daisy-chain-like supramolecular macrocycle, or will it polymerize noncovalently[2b] to generate a macromolecular daisy chain?

An inspection of molecular models convinced us that **1**-H$^+$, a dibenzo[24]crown-8 (DB24C8) derivative bearing a secondary dialkylammonium[9] sidearm, would be a suitable plerotopic monomer for an initial investigation. The question then posed was: would **1**-H$^+$ self-assemble[10] to generate macrocyclic supramolecular oligomers or acyclic supramolecular polymers (Scheme 1); that is, would the self-complementary cation **1**-H$^+$ congregate into supermolecules or supramolecular arrays?[11] Here we describe the synthesis of cation **1**-H$^+$ and its characterization as a dimeric supramolecular macrocycle—the smallest daisy chain imaginable—in both the gas phase and the solid state by mass spectrometry and X-ray crystallography, respectively.



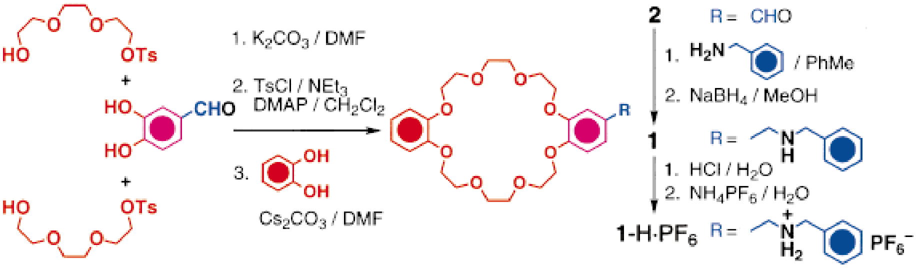
Scheme 1. Cartoon representations of the viable types of self-assembled superarchitectures that can be created from the plerotopic **1**-H$^+$ cation. A) The supramolecular association of a finite number of **1**-H$^+$ monomer units in a cyclic fashion generates oligomeric daisy-chain-like macrocycles. B) The noncovalent polymerization of an infinite number of **1**-H$^+$ monomer units furnishes a supramolecular array that is commensurate with a macromolecular daisy chain.

Scheme 2 outlines the synthesis of **1**-H$^+$ as its hexafluorophosphate salt. The requisite aldehydic precursor of **1**-H · PF$_6$, (2-formyl)dibenzo[24]crown-8 (**2**), was prepared in 17% overall yield from 3,4-dihydroxybenzaldehyde, catechol, and triethylene glycol monotosylate.[12] Reductive amination of **2** with benzylamine furnished **1**, which was transformed into **1**-H · PF$_6$ by protonation with hydrochloric acid followed by counterion exchange from chloride to hexafluorophosphate.

The liquid secondary ion (LSI) mass spectrum[13] of **1**-H · PF$_6$ revealed intense peaks at $m/z = 1281$ and 1135, corresponding to the creation of dimeric supermolecules in the gas phase. These peaks can be identified as the supramolecular ions $[(\mathbf{1}\text{-H})_2(\mathrm{PF_6})]^+$ and $[(\mathbf{1}\text{-H})(\mathbf{1})]^+$, respectively, and indicate the aggregation of two monomer units. Interestingly, the peak at $m/z = 1135$ is the base; it is approximately twice as intense as the peak at $m/z = 568$, which corresponds to $[\mathbf{1}\text{-H}]^+$. However, the isotope peaks were separated by 0.5 mass units around this lower mass peak, thus providing evidence for the existence of the doubly charged dimer $[(\mathbf{1}\text{-H})_2]^{2+}$ in the gas phase. Moreover, the fact that no higher order oligomers could be detected in the mass spectrum confirmed the integrity of the dimer in the gas phase.[14]

In accord with the LSI-MS studies, the X-ray crystallographic analysis[15] of **1**-H · O$_2$CCF$_3$ (Figure 2) reveals the formation of a two-component daisy-chain-like supermacrocycle, possessing C_2 symmetry,[16] in which the $\mathrm{NH_2^+}$-containing sidearms of each component are threaded simultaneously through the complementary DB24C8 recognition sites of their counterparts. This supermolecule is stabilized by a combination of π–π stacking between the $\mathrm{NH_2^+}$-bearing catechol rings (interplanar separation 3.36, centroid–centroid separation 3.55 Å) and hydrogen bonds involving one of the hydrogen atoms on each $\mathrm{NH_2^+}$ group and a polyether oxygen atom from each DB24C8 component ($\mathrm{N^+ \cdots O}$ 2.91, $\mathrm{H \cdots O}$ 2.02 Å; $\mathrm{N^+\text{-}H \cdots O}$ 170°).

An investigation of the packing of the supermolecules (Figure 3) reveals the formation of a mosaiclike[17] sheet composed of enantiomeric dimer pairs $[(\mathbf{1}\text{-H})_2]^{2+}$. This supramolecular sheet self-assembles in one direction by face-to-face π stacking of the terminal phenyl groups of each monomer (interplanar separation 3.62, centroid–centroid separation 3.73 Å), supplemented by edge-to-face interactions between these pairs of interacting terminal rings and the



Scheme 2. Synthesis of the plerotopic salt **1**-H · PF$_6$. Ts = *p*-toluenesolufonyl, DMAP = 4-dimethylaminopyridine.

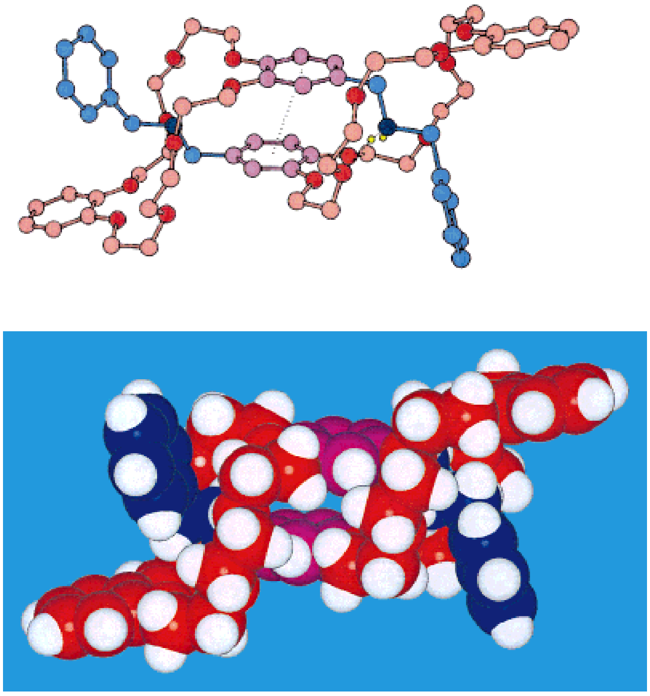


Figure 2. The crystal structure of the supermolecule $[(\mathbf{1}\text{-H})_2]^{2+}$, which may be classed as a [*c*2]daisy chain (*c* designates[8] that the daisy chain is cyclic, while the 2 symbolizes the number of components of which it is composed). Top: Ball-and-stick representation. Bottom: Space-filling representation. Blue: Secondary dialkylammonium sidearms; magenta: sidearm-bearing catechol rings; red: polyether loops and unsubstituted catechol rings.

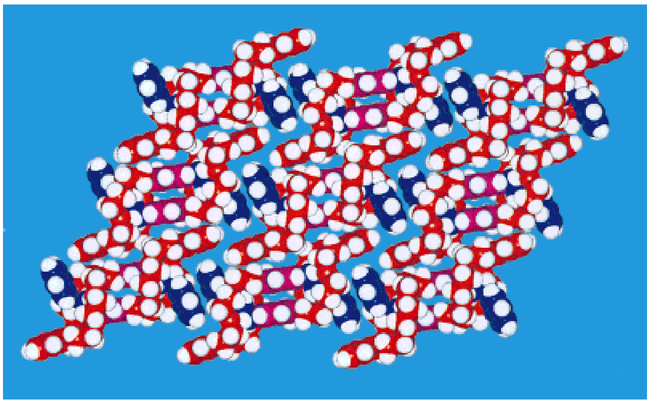


Figure 3. Space-filling representation of the mosaiclike sheet comprised of enantiomeric $[(\mathbf{1}\text{-H})_2]^{2+}$ supermolecules.

immediately adjacent unsubstituted catechol rings of contiguous dimer pairs (centroid–centroid separation 5.06 Å, rings being inclined by 83° to each other). Neighboring rows of supermolecules are then aligned such that pairs of the OCH_2 hydrogen atoms within the polyether linkages in one π-stacked row are directed from above and below into the π faces of the already π–π stacked substituted catechol rings within each dimer ($H\cdots\pi$ 2.69 Å, $C\text{-}H\cdots\pi$ 161°). Channels which are populated by $CF_3CO_2^-$ counterions and CF_3CO_2H molecules are created between each sheet.

The self-assembly of the finite [*c*2]daisy chain $[(\mathbf{1}\text{-H})_2]^{2+}$ demonstrates[18] that it is extremely difficult to overcome the enthalpic and entropic costs of generating infinite supramolecular arrays in noncovalent syntheses which operate under thermodynamic control. Nevertheless, the research presented here is an initial step along the road to a novel range of molecular and supramolecular polymers. By way of illustration, one can envisage functionalized [*c*2]daisy chain superarchitectures undergoing condensation polymerization reactions with difunctional spacer units to generate novel mechanically interlocked molecular polymers.[19] Moreover, it can be imagined that replacement of the $\mathbf{1}\text{-H}^+$ cation's substituted catechol unit—which is involved in stabilizing π–π stacking interactions in the supermolecule $[(\mathbf{1}\text{-H})_2]^{2+}$ (see above)—with a bulky, sterically cumbersome unit, that cannot enter into π–π stacking interactions, could lead to the supramolecular syntheses of acyclic [*a*∞]daisy chain supramolecular polymers that are composed of an infinite number of monomer units. Indeed, it may be that the "stoppering"[20] of such species could lead, ultimately, to unique mechanically interlocked polymers,[19] namely, macromolecular daisy chains.

Experimental Section

2: Reaction of 3,4-bis[2-(2-(2-*p*-toluenesulfonyloxy)ethoxy)ethoxy)ethoxy]benzaldehyde[21] (8.43 g, 11.9 mmol) with catechol (1.31 g, 11.9 mmol) in the presence of Cs_2CO_3 (19.30 g, 59.3 mmol) in DMF (700 mL) at 100 °C furnished, after standard extractive workup with PhMe and 1 N HCl, a crude product, which was subjected to column chromatography (SiO_2; gradient elution with EtOAc/MeOH, 100/0 → 95/5). The ensuing material was recrystallized from EtOAc/nC_6H_{14} to provide **2** (2.31 g, 41 %) as a white solid. M.p. 105–107 °C; ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 3.82-3.85$ (m, 8 H), 3.89–3.97 (m, 8 H), 4.12–4.24 (m, 8 H), 6.83–6.90 (m, 4 H), 6.93 (d, $J = 8.1$ Hz, 1 H), 7.37 (d, $J = 1.8$ Hz, 1 H), 7.42 (dd, $J = 8.1$, 1.8 Hz, 1 H), 9.81 (s, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): $\delta = 69.4$, 69.5, 69.7, 70.0, 71.3, 71.4, 71.5, 111.1, 111.9, 114.0, 121.4, 126.8, 130.2, 148.9, 149.2, 154.3, 190.9; MS (LSI): $m/z = 477$ $[M+H]^+$; calcd for $C_{25}H_{32}O_9$ (476.5): C 63.01, H 6.77; found: C 63.12, H 6.54.

$\mathbf{1}\text{-H}\cdot PF_6$: Reductive amination of **2** (1.50 g, 3.2 mmol) with $PhCH_2NH_2$ (0.34 g, 3.2 mmol) by standard procedures[2b, 9] afforded the amine **1** (1.42 g, 79 %) as a pale yellow oil [^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 3.71$ (s, 2 H), 3.77 (s, 2 H), 3.82 (s, 8 H), 3.88–3.93 (m, 8 H), 4.11–4.17 (m, 8 H), 6.78–6.91 (m, 5 H), 7.20–7.34 (m, 7 H)]. According to a typical protocol,[9] a portion of **1** (0.47 g, 0.8 mmol) was then allowed to react with 5 N HCl (50 mL) to furnish, after counterion exchange with NH_4PF_6, $\mathbf{1}\text{-H}\cdot PF_6$ (0.55 g, 93 %) as a white powder. M.p. > 210 °C (decomp); ^1H NMR (300.1 MHz, $(CD_3)_2SO$, 20 °C): $\delta = 3.68$ (s, 8 H), 3.74–3.83 (m, 8 H), 4.04–4.16 (m, 12 H), 6.86–6.99 (m, 4 H), 7.02 (s, 2 H), 7.13 (s, 1 H), 7.47 (br s, 5 H), 9.09 (br s, 2 H); ^{13}C NMR (75.5 MHz, $(CD_3)_2SO$, 20 °C): $\delta = 49.9$, 50.0, 68.7, 69.0, 69.1, 70.4, 113.5, 114.0, 115.4, 121.1, 123.0, 124.2, 128.7, 129.0, 129.9, 132.0, 148.2, 148.4, 148.9; MS (LSI): $m/z = 1135$ $[2M - HPF_6 - PF_6]^+$; calcd for $C_{32}H_{42}NO_8PF_6$ (713.6): C 53.86, H 5.93, N 1.96; found: C 53.60, H 5.84, N 2.05.

Received: December 29, 1997 [Z 11292 IE]
German version: *Angew. Chem.* **1998**, *110*, 1344–1347

Keywords: crown compounds · host–guest chemistry · noncovalent interactions · self-assembly · supramolecular chemistry

---

[1] a) G. Schill, *Catenanes, Rotaxanes, and Knots*, Academic Press, New York, **1971**; b) J. C. Chambron, C. O. Dietrich-Buchecker, J.-P. Sauvage, *Top. Curr. Chem.* **1993**, *165*, 131–162; c) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; d) R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 966–980; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 930–944.

[2] a) P. R. Ashton, A. N. Collins, M. C. T. Fyfe, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1997**, *109*, 760–763; *Angew. Chem. Int.*

Ed. Engl. **1997**, *36*, 735–739; b) P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 577–589.

[3] a) J.-M. Lehn, *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1–17; b) G. M. Whitesides, E. E. Simanek, J. P. Mathias, C. T. Seto, D. N. Chin, M. Mammen, D. M. Gordon, *Acc. Chem. Res.* **1995**, *28*, 37–44.

[4] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**, pp. 161–165.

[5] D. B. Amabilino, I. W. Parsons, J. F. Stoddart, *Trends Polym. Sci.* **1994**, *2*, 146–152.

[6] a) J. L. Sessler, A. Andrievsky, P. A. Gale, V. Lynch, *Angew. Chem.* **1996**, *108*, 2954–2957; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2782–2785; b) A. Zanotti-Gerosa, E. Solari, L. Giannini, A. Chiesa-Villa, C. Rizzoli, *Chem. Commun.* **1996**, 119–120; c) M. Dimitrius, A. Terzius, A. W. Coleman, C. de Rango, *Carbohydr. Res.* **1996**, *282*, 125–135; d) M. Asakawa, P. R. Ashton, C. L. Brown, M. C. T. Fyfe, S. Menzer, D. Pasini, C. Scheuer, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 1136–1150.

[7] P. R. Ashton, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gómez-López, S. Iqbal, D. Philp, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1997**, *3*, 152–170.

[8] The term "daisy chain" is defined in *Webster's Third New International Dictionary* (Ed.: P. Babcock-Gove), Merrian-Webster, Springfield MA, **1993**, as "a string of daisies with stems linked to form a chain, … such a chain carried by chosen students at a class day or other celebration in some women's colleges." A daisy chain may be acyclic [*a*]—that is, linear, as shown in Figure 1—or it may have its ends linked together to afford a cyclic [*c*] assembly; thus, a [*c*]daisy chain resembles a necklace. In the molecular world, an [*a*]daisy chain has a free pair of potentially matching recognition sites, whereas a [*c*]daisy chain experiences maximal occupancy of its recognition sites (see ref. [4], pp. 182–183), following the closure of an [*a*]daisy chain using its last pair of complementary recognition sites located at the termini of the growing chain.

[9] P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, C. Schiavo, N. Spencer, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709–728.

[10] a) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229–2260; b) D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196; c) M. M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647–1668; d) B. Linton, A. D. Hamilton, *ibid.* **1997**, *97*, 1669–1680.

[11] M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401.

[12] L. Börjesson, C. J. Welch, *Acta Chem. Scand. Ser. B* **1991**, *45*, 621–626.

[13] The spectrum was obtained with a VG Zabspec mass spectrometer (positive-ion mode at a scan speed of 10 s per decade) equipped with a cesium ion source and utilizing a *m*-nitrobenzyl alcohol matrix.

[14] However, the solution-phase behavior of **1**-H·PF_6 was not as straightforward as that in the gas phase. The ^1H NMR spectrum (400.1 MHz, CD_3CN with a drop of D_2O, 0 °C) of **1**-H·PF_6 was extremely complicated as a result of various aggregation–deaggregation phenomena occurring simultaneously. This spectrum gradually simplified, indicating the presence of completely disassociated **1**-H^+, when the temperature was increased stepwise to 80 °C. A simple ^1H NMR spectrum was also obtained in $(CD_3)_2SO$, a solvent that has a strong preference[9] for entering into hydrogen bonds with secondary dialkylammonium ions and which consequently disfavors intermolecular interactions between distinct units of **1**-H^+.

[15] The salt **1**-H·O_2CCF_3 was prepared by allowing **1** to react with an excess of CF_3CO_2H in CH_2Cl_2 and then removing the solvent under reduced pressure. Single crystals suitable for X-ray crystallographic analysis were obtained when a solution of the salt in EtOAc/$n$$C_6H_{14}$/MeCN was allowed to stand at 20 °C for about 1 d. Crystal data for $[C_{32}H_{42}NO_8][O_2CCF_3]\cdot CF_3CO_2H$: $M_r = 795.7$, monoclinic, space group $C2/c$, $a = 22.936(4)$, $b = 23.249(3)$, $c = 15.393(3)$ Å, $\beta = 112.14(1)^\circ$, $V = 7603(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.39$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.22$ cm^{-1}, $F(000) = 3328$. Crystal dimensions $0.33 \times 0.33 \times 0.80$ mm (needles), Siemens P4 diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, ω-scans, $T = 203$ K. Of 6449 independent reflections measured ($2\theta \leq 50^\circ$), 2715 had $I_0 > 2\sigma(I_0)$ and were considered to be observed. The structure was solved by direct methods, and the major occupancy non-hydrogen atoms refined anisotropically. The positions of the NH_2^+ hydrogen atoms were located from a ΔF map and refined isotropically subject to an N−H distance constraint. The remaining hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent atoms. Refinement was by full-matrix least squares based on F^2 to give $R_1 = 0.092$ and $wR_2 = 0.222$. Computations were carried out with the SHELXTL 5.03 package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] Interestingly, in this instance, the interaction between the two achiral **1**-H^+ cations is dissymmetrizing, rendering a chiral association and resulting in the formation of a pair of enantiomeric C_2-symmetric supramolecular stereoisomers. This kind of interaction occurs because the enantiotopic faces of the interacting **1**-H^+ cations possess the same prochirality. However, an alternative situation can also be envisaged: A diastereoisomeric "*meso*" supramolecular stereoisomer—endowed with C_i symmetry—would have been created if the interacting faces of individual **1**-H^+ cations had maintained different prochiralities upon crystallization. In other words, the noncovalent dimerization of the **1**-H^+ cation proceeds diastereoselectively, at least in the solid state, to furnish a racemic mixture of the C_2-symmetric supramolecular stereoisomers.

[17] P. R. Ashton, C. G. Claessens, W. Hayes, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1995**, *107*, 1994–1997; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1862–1865.

[18] a) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398; b) P. R. Ashton, A. N. Collins, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1997**, *109*, 59–62; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 59–62; c) D. L. Caulder, K. N. Raymond, *ibid.* **1997**, *109*, 1508–1510 and **1997**, *36*, 1440–1442.

[19] S. Menzer, A. J. P. White, D. J. Williams, M. Belohradsky, C. Hamers, F. M. Raymo, A. N. Shipway, J. F. Stoddart, *Macromolecules* **1998**, *31*, 295–307.

[20] P. R. Ashton, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 729–736.

[21] S. J. Cantrill, MPhil Thesis, University of Birmingham (UK), **1997**.