formic acid (Ph_3P, DEAD, C_6H_6; >90% yield based on consumed starting material), although the reaction could not be pressed beyond 40% conversion. The product was quantitatively converted to baccharin B5 (**1**) by deformylation/desilylation with Bu_4NF/THF. Our synthetic material was identical by all the usual criteria including ^{13}C NMR with a sample of the natural **1** generously supplied by Dr. Matthew Suffness of NIH and Dr. Fred Boettner of Polysciences.

The synthesis of baccharin described here is an application of macrocyclically controlled remote asymmetric induction to complex natural product synthesis. It not only provides a simple route to the baccharinoids but also illustrates that potential of remote asymmetric induction strategies in organic synthesis.[13]

Supplementary Material Available: Full NMR, IR, and mass spectral data for compounds **3–11** (7 pages). Ordering information is given on any current masthead page.

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(12) Review: Mitsunobu, O. *Synthesis* **1981**, *1*.

(13) This work was supported by NIH Grant GM32598.

Crystal Structures of Azoarene-Capped Analogues of 1,10-Diaza-4,7,14,17-tetraoxa- and 1,10-Diaza-4,7,14,17-tetrathiacyclooctadecane. Comparison of C–O and C–S Bond Conformations in Capped Crown Analogues

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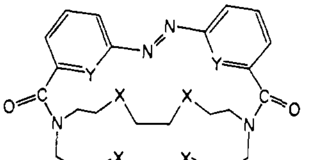
Macropolycyclic polyethers contain intramolecular cavities lined with molecular segments capable of binding cations in three-dimensional cagelike structures. The Azoarene-capped O and S crown ethers (e.g., **1–3**) undergo photoinduced reversible interconversion between the trans and cis azo linkages, resulting in substantial changes in their cation binding properties.[3] The X-ray structures of the azopyridine-capped analogue of 1,10-diaza-18-crown-6 (**1**) and the azobenzene-capped sulfur analogue (**3**) have been determined as a step in understanding how ion selectivity and binding are controlled by the cavity structure. The conformations of the crown rings in **1** and **3** are substantially different from those of the "free" analogues, the latter containing the first example of the C–S anti conformation in a thiacrown macrocycle.



1, X = O; Y = N
2, X = S; Y = N
3, X = S; Y = CH

X-ray quality crystals of **2** could not be obtained. X-ray data: Picker FACS-I diffractometer, graphite monochromator, Cu Kα $\lambda = 1.5418$ Å; 2θ–θ intensity scan, 10-s backgrounds, $2\theta = 126°$.

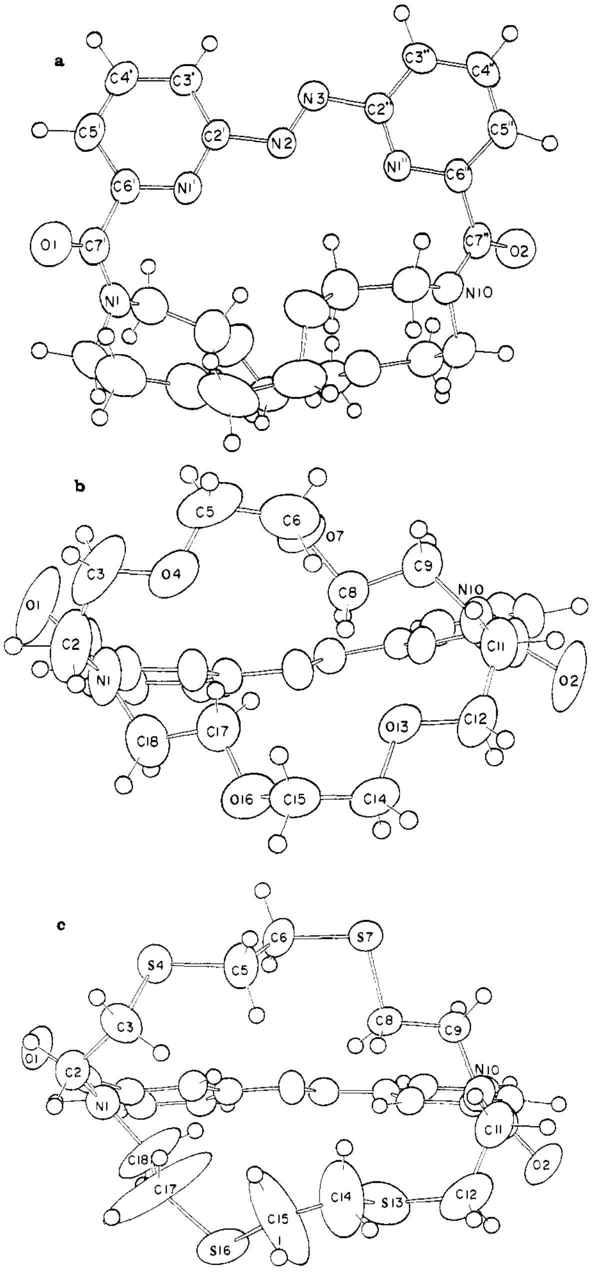


Figure 1. ORTEP drawings of **1** and **3**. The C, N, O, and S atoms are illustrated as 50% probability ellipses, and the H atoms are 0.1-Å radius circles. (a) **1** viewed perpendicular to the azopyridine moiety. (b) **1** viewed parallel to the azopyridine moiety. (c) **3** viewed parallel to the azobenzene moiety.

Crystal data: **1**, $C_{24}H_{30}N_6O_6$, M_r 498, 0.033 × 0.26 × 0.41 mm crystal (toluene), $C2/c$, $a = 43.126$ (4) Å, $b = 7.9747$ (4) Å, $c = 14.367$ (1) Å, $\beta = 93.45$ (2)°, $Z = 8$, $\rho_{\rm Xray} = 1.341$ g cm^{-3}, 3995 unique reflections, 2936 with $I > 3\sigma(I)$; **3**, $C_{26}H_{32}N_4O_2S_4$, $M_r = 560$, 0.3 × 0.20 × 0.25 mm crystal (methylene chloride–chlorobenzene), $P2_1/a$, $a = 10.766$ (1) Å, $b = 23.552$ (2) Å, $c = 11.569$ (1) Å, $\beta = 111.057$ (4), $Z = 4$, $\rho_{\rm Xray} = 1.361$ g cm^{-3}, 4431 unique reflections, 2873 with $I > 3\sigma(I)$. Block-diagonal, least-squares refinement of $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$. Final $R(\sum|F_o - F_c|/\sum F_o)$ and weighted R $([\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2})$ values are 0.052 and 0.051 for **1** and 0.076 and 0.057 for **3**[4] (atomic coordinates and temperature factors are given in the supplementary material).

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(3) Shinkai, S.; Nakaji, T.; Nishida, Y.; Ogawa, T.; Manabe, O. *J. Am. Chem. Soc.* **1980**, *102*, 5860–5865. Shinkai, S.; Kouno, T.; Kusano, Y.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1982**, 2741–2747.

(4) UNIVAC 1100/82 computer. Crystallographic programs: Stewart, J. M.; Machin, P. A.; Dickinson, C.; Ammon, H. L.; Heck, H. S.; Flack, H. The X-ray 76 System of Crystallographic Programs, Tecnical Report 446, 1976, Computer Science Center, University of Maryland, College Park, MD.

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The azoarene cap-crown ring angles are 82.5° in **1** and 79.3° in **3** (Figure 1a–c). Bond lengths in **1** are normal. There are some distorted distances in **3**[5] as a result of possible disorder in a portion of the thiacrown ring. The transannular N···N distances of 7.83 Å in **3** and 7.09 Å in **1** reflect differences in the C–S and C–O bond lengths. Two of the four crown oxygen atoms in **1** are endodentate and two are exodentate, whereas all four of the crown sulfurs in **3** are exodentate.

The conformations of the crown rings in **1** and **3** differ considerably from those observed in the uncapped analogues, 18-crown-6[7] and hexathia-18-crown-6.[6] The ring conformations,[8] $(g^+\mathrm{g^-a,ag^+a,g^-a}g^-)(g^+\mathrm{g^-a,ag^+g^-,aa}g^-)$ in **1** and $\mathrm{(g^+g^-a,ag^+a,aaa)(g^-g^+a,ag^-a,aaa)}$ in 18-crown-6,[6,7] both illustrate the preference of the C–O linkage for the anti conformation. The hexathia-18-crown-6 conformation[6] of $\mathrm{(g^+ag^-,g^+g^+g^-,g^+ag^+)_2}$ has an abundance of gauche conformations compared to the oxy analogue and no C–S anti conformations. By contrast, the $(g^+\mathrm{g^+a,aag^+,aa}g^-)(a\mathrm{g^-g^-,ag^-g^{-\prime},g^+a}g^+)$ conformation of **3** shows that *four of the eight C–S bonds adopt the anti conformation.*[10] The compound is the first thiacrown to exhibit the C–S anti conformation. In discussing the prevalence of the C–S gauche and C–O anti conformations in crown compounds, Hartman et al.[6] suggested that C–S bonds are sufficiently longer than C–O bonds that 1,4-steric interactions no longer disfavor the C–S gauche conformation. While this may be the case for unrestricted thiaethers such as the 18-crown-6 analogue, the azobenzene cap in **3** must impose additional conformational constraints on the crown ring.

We previously found that 1,10-diaza-18-crown-6 capped with *trans*-azobenzene (X = O and Y = CH) preferentially binds Li^+ and Na^+, whereas the cis form prefers the larger K^+ and Rb^+.[3] There is evidence that the crown ring in 18-crown-6–metal complexes adopts the all-gauche C–C conformation with D_{3d} symmetry in solution as well as in the crystalline state.[11] The crystal structure of **1** shows that two of the six crown C–C bonds are anti and that the ring is oval shaped. Because the azoarene cap in **1** confers a certain degree of conformational rigidity on the crown ring, it is expected that differences between the uncomplexed and cation-complexed conformations will be appreciably smaller than those observed in the uncapped crowns. These conformational and shape factors are probably why **1** favors Li^+ and Na^+, which are smaller than the cavity size of the all-gauche C–C, K^+-preferring, 18-crown-6.

We have also observed that trans-capped **1** is capable of binding heavy metal ions, whereas **1** with the photoisomerized cis cap has little affinity for these cations. The structure of **1** shows that the *trans*-azopyridine moiety stands vertically over the crown ring and suggests that the pyridine ring nitrogens should be capable of coordinating to metal ions bound by the crown polyether ring. Such a three-dimensional coordination geometry would be unexpected for cis-capped **1** because the pyridine rings are likely to be parallel to the crown plane.[3] An additional factor that undoubtedly contributes to decreased cation binding by the cis-capped isomer is the substantial change in the crown ring structure that must accompany the trans to cis conversion.

Further investigations of the three-dimensional crowns will undoubtedly reveal other differences with the two-dimensional analogues. Investigations delineating the photoinduced conformational changes accompanying the trans to cis interconversions in the three-dimensional crowns will be of particular importance, as well as studies of the relationships between the cavity and cation-guest structures.

Acknowledgment. This work was supported, in part, through the facilities of the University of Maryland's Computer Science Center.

Registry No. **1**, 81963-40-8; **2**, 88180-94-3; **3**, 88180-93-2; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8.

Supplementary Material Available: Tables of atomic coordinates and temperature factors and of bond lengths (3 pages). Ordering information is given on any current masthead page.

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(5) Possible positional disorder also was reported in hexathia-18-crown-6.[7]

(6) Hartman, J. R.; Wolf, R. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 131–132.

(7) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1980**, *B36*, 615–620.

(8) The ring conformations are specified by the torsion angles[9] about the various XCH_2CH_2Y (X, Y = N, O, or S) fragments. The torsion angle sequences given in ref 6 are for the ECH_2CH_2E (E = O or S) fragments, and not for the $CH_2ECH_2CH_2$ arrangement indicated in the reference.

(9) Dale, J. *Isr. J. Chem.* **1980**, *20*, 3–11. g^+ and g^- indicate gauche conformations (torsion angles of 0° to +120° and 0° to −120°); a indicates the antiperiplanar conformation (± 120° to 180°); $g^{\pm\prime}$ indicates a torsion angle of ±120°. In the case of the capped molecules, italic letters (e.g., *g* or *a*) refer to the C–N conformation.

(10) The C–S torsion angles in **3**, clockwise from N1 (Figure 1c), are −136.3 (4)°, 163.9 (5)°, 67.5 (6)°, 156.5 (4)°, −92.3 (5)°, −163.3 (8)°, −120 (1)°, 113 (1)°.

(11) Live, D.; Chan, S. I. *J. Am. Chem. Soc.* **1976**, *98*, 3769–3778. Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect B* **1973**, *B29*, 589–595. Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerly *Ibid.* **1974**, *B30*, 2733–2738. Goldberg, I. *Ibid.* **1975**, *B31*, 754–762.

Carbon Monosulfide Chemistry in Solution. Insertion into Sulfur–Chlorine Bonds

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Several years ago one of us reported that carbon monosulfide (CS) could be prepared on a synthetic scale by passing CS_2 through a high-voltage discharge.[2,3] In the gas phase CS could be moved considerable distances in a vacuum system and codeposited at liquid nitrogen temperature yielding frozen CS monomer as a white solid. Upon slight warming violent polymerization took place yielding light, heat, and an insoluble $(CS)_n$ polymer. (Caution: the isolation of large amounts of CS monomer can be dangerous due to the violent nature of this polymerization process.)

Using codeposition techniques[4] we found that CS was relatively unreactive with most coreagents, presumably due to the competing highly favored polymerization process.[2] We have now found that CS can serve as a useful synthon when solution-phase reactions are employed. Due to the considerable potential of CS as an organic reagent and as a ligand in organometallic chemistry,[5] we have begun to expand our efforts in this area.

The production of CS was carried out using conventional vacuum line techniques by passing pure CS_2 through a high-voltage ac discharge.[2]. Sulfur was quickly deposited along with some $(CS)_n$ polymer. However, the bulk of the CS passed out of the discharge region; a portion will even pass through a −114 °C U-trap. Continual operation of the discharge for several hours allowed the production of 5–10 g of CS.

$$\mathrm{CS_2} \xrightarrow{\text{4–8 kV}} \mathrm{CS + S} \rightarrow \mathrm{S}_n$$

$$\mathrm{CS(g)} \xrightarrow{\text{slow}} \mathrm{(CS)}_n$$

The $(CS)_n$ polymer continually deposited on the walls of the flow system and reaction flask. Some CS monomer was trapped in the −196 °C copper cold trap following the reaction flask and upon slight warming small, nondestructive explosions took place.

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(1) (a) Kansas State University. (b) Aarhus University.

(2) Klabunde, K. J.; White, C. W.; Efner, H. F. *Inorg. Chem.* **1974**, *13*, 1778.

(3) For reviews dealing with CS, see: Gattow, G.; Behrendt, W., *Top. Sulfur Chem.* **1977**, *2*, 1. White, C. W. Masters Thesis, University of North Dakota, Grand Forks, ND, 1974.

(4) Klabunde, K. J. "Chemistry of Free Atoms and Particles"; Academic Press: New York, 1980; p 191.

(5) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.

0002-7863/84/1506-0263$01.50/0