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] $(g^{+}\mathrm{g}^{-}\mathrm{a},\mathrm{ag}^{+}\mathrm{a},\mathrm{g}^{-}\mathrm{a}g^{-})(g^{+}\mathrm{g}^{-}\mathrm{a},\mathrm{ag}^{+}\mathrm{g}^{-},\mathrm{aa}g^{-})$ in **1** and $(\mathrm{g}^{+}\mathrm{g}^{-}\mathrm{a},\mathrm{ag}^{+}\mathrm{a},\mathrm{aaa})(\mathrm{g}^{-}\mathrm{g}^{+}\mathrm{a},\mathrm{ag}^{-}\mathrm{a},\mathrm{aaa})$ 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 $(\mathrm{g}^{+}\mathrm{ag}^{-},\mathrm{g}^{+}\mathrm{g}^{+}\mathrm{g}^{-},\mathrm{g}^{+}\mathrm{ag}^{+})_2$ has an abundance of gauche conformations compared to the oxy analogue and no C–S anti conformations. By contrast, the $(g^{+}\mathrm{g}^{+}\mathrm{a},\mathrm{aag}^{+},\mathrm{aa}g^{-})(a\mathrm{g}^{-}\mathrm{g}^{-},\mathrm{ag}^{-}\mathrm{g}^{-\prime},\mathrm{g}^{+}\mathrm{a}g^{+})$ 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.

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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 $\mathrm{XCH_2CH_2Y}$ (X, Y = N, O, or S) fragments. The torsion angle sequences given in ref 6 are for the $\mathrm{ECH_2CH_2E}$ (E = O or S) fragments, and not for the $\mathrm{CH_2ECH_2CH_2}$ 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°); $\mathrm{g}^{\pm\prime}$ 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

Kenneth J. Klabunde,*[1a] Michael P. Kramer,[1a]
Alexander Senning,*[1b] and Ejner K. Moltzen[1b]

Departments of Chemistry, Kansas State University
Manhattan, Kansas 66506
Aarhus University
DK-8000 Aarhus C, Denmark

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Several years ago one of us reported that carbon monosulfide (CS) could be prepared on a synthetic scale by passing $\mathrm{CS_2}$ 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 $(\mathrm{CS})_n$ 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 $\mathrm{CS_2}$ through a high-voltage ac discharge.[2]. Sulfur was quickly deposited along with some $(\mathrm{CS})_n$ 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.

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

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

The $(\mathrm{CS})_n$ 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.

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If CS was passed into a cold (−80 °C), stirred toluene solution,[6] fine particles of brown-black $(\mathrm{CS})_n$ precipitated.

A stirred solution of benzenesulfenyl chloride in toluene reacted efficiently and without $(\mathrm{CS})_n$ formation at −50 °C to yield the S–Cl insertion product phenyl chlorodithioformate (**1**).[7,8] (The

$$\mathrm{CS} + \mathrm{C_6H_5SCl}\ (4{:}1) \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{\mathrm{C_6H_5SC({=}S)Cl}}$$

solution-phase experiments were carried out as previously described with the noteable exception of using excess CS to substrate rather than the reverse.[2] Typically the experiments required 1.5 h to inlet 25 mL of $\mathrm{CS_2}$ through the discharge.)

The yield of **1** is high and treatment of the solution with excess CS led to $(\mathrm{CS})_n$ polymer formation. Thus, the benzenesulfenyl chloride could be titrated with CS until the dark $(\mathrm{CS})_n$ solid began to form. This observation indicates that the C–S and C–Cl bonds in the product are inert to further reaction with CS under these conditions.

This constitutes the first example of a CS insertion into a S–Cl bond and is the first example of the isolation of a primary reaction product from a CS reaction. The possibilities for the production of new compounds are substantial. For example, we have investigated $\mathrm{S_2Cl_2}$ in cold toluene solution. In this case all of the CS was absorbed leading to a novel double insertion product, dithiobis(thiocarbonyl chloride)(**2**).[9]

$$\mathrm{CS} + \mathrm{S_2Cl_2} \xrightarrow[-70\ ^\circ\mathrm{C}]{\text{toluene}} \underset{\mathbf{2}}{\mathrm{ClC({=}S)SSC({=}S)Cl}}$$

Compound **2**, a novel compound inaccessible by other methods, was trapped with diethylamine in a carbon tetrachloride solution to give the known tetraethylthiuram disulfide.[10a,b]

$$\mathbf{2} + 2\mathrm{Et_2NH} \xrightarrow[+5\ ^\circ\mathrm{C}]{\mathrm{CCl_4}} \mathrm{Et_2NC({=}S)SSC({=}S)NEt_2} + 2\mathrm{HCl}$$

Compound **2** exhibits one $^{13}\mathrm{C}$ NMR absorption downfield from $\mathrm{CDCl_3}$ at 189.4 ppm, consistent with reported values for other thioacid chlorides;[11] IR (neat, $\mathrm{cm^{-1}}$) displays product bands at 740 and 1120 that have been assigned to C—Cl and C═S stretches, respectively. Mass spectral data confirm the expected masses and isotope patterns for compound **2**: MS (CI) M = $\mathrm{S_4Cl_2C_2^+}$ (45%), $\mathrm{S_3Cl_2C_2^+}$ (34%), $\mathrm{S_3Cl_2C^+}$ (16%), $\mathrm{S_2Cl_2C_2^+}$ (43%), $\mathrm{S_2Cl_2^+}$ (59%), $\mathrm{S_2Cl_2^+}$ (75%), $\mathrm{S_2ClC^+}$ (78%), $\mathrm{S_2Cl^+}$ (100%), $\mathrm{CS_2^+}$ (68%), $\mathrm{S_2^+}$ (27%).

Since some $\mathrm{S_2Cl_2}$ was still present after formation of **2**, the monoinsertion product must exhibit higher reactivity toward CS than $\mathrm{S_2Cl_2}$:

$$\mathrm{S_2Cl_2} \rightarrow \underset{\mathbf{3}}{\mathrm{ClSSC({=}S)Cl}} \rightarrow \mathbf{2}$$

Although we do not understand why **3** should have such high reactivity, we note that $\mathrm{S_2Cl_2}$ is not highly reactive with CS, and it appears that at low temperatures CS can be solvated by $\mathrm{S_2Cl_2}$ prior to S–Cl insertion.

Further studies of CS reactivity and its use as a synthon are under way.

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(6) Toluene was chosen as a solvent mainly because of its low melting point, relative unreactivity, low vapor pressure, and favorable fluid properties under low-temperature conditions.

(7) Rivier, H. *Bull. Soc. Chim. Fr.* **1907**, *1* (4), 737.

(8) The yield of compound **1** is based on the starting benzenesulfenyl chloride and varies from 25% to 80% depending on the reaction conditions and workup. A typical yield is 73% isolated by distillation.

(9) Only the double insertion product is observed in the IR and the yield of this reaction varies with reaction conditions as well as workup conditions. A typical yield, based on $\mathrm{S_2Cl_2}$, is 50% (isolated by vacuum evaporation of the solvent). We have purified **2** by vacuum distillation, although some decomposition occurred. In all cases liquid **2** contained no $\mathrm{CS_2}$ as an impurity as shown by IR analysis.

(10) (a) Florey, K. "Analytical Profiles of Drug Substances"; Academic Press: New York, San Francisco, London, 1975; Vol. 4, p 169. (b) The IR, mass spectra, $^{13}\mathrm{C}$ NMR, and melting point all correlated with the known compound. A yield of 10.0% was isolated based on **2**.

(11) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden & Son Ltd.: London, Philadelphia, Rheine, 1978; Carbon-13 Correlation Chart.

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*Book Reviews**

Mineral Effects in Coal Conversion. By Robert M. Davidson. IEA Coal Research, London SW1W OEX. 1983. 100 pp. £10.00.

This Report is the product of the Technical Information Service of the International Energy Agency. It is a review, with 256 references, of recent research on pyrolysis of coal, hydrogenation of coal to produce liquid fuels, liquefaction with carbon monoxide, heteroatom removal, and oxidative gasification, from the standpoint of the influence of inorganic matter, especially pyrite, present in coal. The bibliography is particularly useful because of its wide range; it includes reports and preprints, as well as periodical publications. The period covered is 1974–1982.

Chromatography of Alkaloids. By A. Baerheim Svendsen and R. Verpoorte. Elsevier Scientific Publishing Company, Amsterdam and New York. 1983. xvi + 536 pp. $104.25.

The first of a two-volume set (the second will cover GLC and HPLC techniques), this book comprehensively reviews the literature on TLC of alkaloids (about 1800 references through the late 1970's). The first (General) part of the book describes available systems and techniques as well as general methods of detection, separation, identification, and isolation of alkaloids. It includes a short discussion of the relationships between solvents, alkaloid stability, and artefact formation. The second (Special) part reviews TLC of the particular alkaloids, grouping them in sections according to their chemical skeletons. Sections may be further divided as necessary. For example, there are special chapters on ergot and *Psilocybe* (indole) alkaloids. The chapter covering the opium alkaloids includes many methods of detecting drugs of abuse and should be of interest to clinicians and forensic scientists. At the end of each chapter are numerous tables describing systems of separation, methods of detection, and special characteristics of the individual alkaloids. An appendix lists preparation and use of over 100 detection methods and spray reagents mentioned in the text.

The book is a necessity for chemistry and pharmacy libraries, and researchers will welcome it, for it should help them get out of the library and into the laboratory (where they may wish to keep their own copy).

L. J. Valdés, *College of Pharmacy, University of Michigan*

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*Unsigned book reviews are by the Book Review Editor.