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# Eight- and 16-Membered Cyanuric−Sulfanuric Ring Systems: $C_2N_4S_2 \rightarrow C_2N_3S$ Ring Contraction

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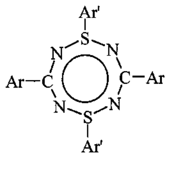
Eight- and 16-membered cyanuric−sulfanuric ring systems of the type $Ar_2C_2N_4S_2(O)_2Ar'_2$ (**3a**, Ar = 4-$BrC_6H_4$, Ar′ = Ph; **3b**, Ar = 4-$CF_3C_6H_4$, Ar′ = Ph; **3c**, Ar = 4-$CF_3C_6H_4$, Ar′ = 4-$CH_3C_6H_4$) and $Ar_4C_4N_8S_4(O)_4Ar'_4$ (**4b**, Ar = 4-$CF_3C_6H_4$, Ar′ = Ph; **4c**, Ar = 4-$CH_3C_6H_4$, Ar′ = Ph; **4d**, Ar = 4-$CF_3C_6H_4$, Ar′ = 4-$CH_3C_6H_4$), respectively, were prepared in good yields by the reaction of the corresponding sulfur(IV) systems with *m*-chloroperbenzoic acid. The X-ray structures of **3b**, **3c**·$C_7H_{14}$, **4b**·$CH_2Cl_2$, **4c**, and the S(IV) system $Ar_4C_4N_8S_4Ar'_4$ (**2c**, Ar = 4-$CH_3C_6H_4$, Ar′ = Ph) were determined. Upon oxidation the two oxygen atoms in **3b** and **3c**·$C_7H_{14}$ adopt endo positions leading to a twist boat conformation for the $C_2N_4S_2$ ring. The 16-membered $C_4N_8S_4$ rings in **4b** and **4c** retain a cradle conformation upon oxidation. The S−N bond distances are ca. 0.06 Å shorter in all the S(VI) systems compared to those in the corresponding S(IV) rings. The thermolysis of **3b** at ca. 220 °C occurs primarily via loss of a sulfanuric group, NS(O)Ph, to give the six-membered ring (4-$CF_3C_6H_4$)$_2C_2N_3S$(O)Ph (**6**). The structure of **6** was confirmed by X-ray crystallography. Crystal data: **2c**, triclinic, space group $P\bar{1}$ with $a = 13.917(2)$ Å, $b = 15.610(4)$ Å, $c = 13.491(3)$ Å, $\alpha = 95.77(2)°$, $\beta = 114.82(1)°$, $\gamma = 76.21(2)°$, $V = 2583(1)$ Å$^3$, and $Z = 2$; **3b**, monoclinic, space group $P2_1/a$ with $a = 7.316(2)$ Å, $b = 29.508(5)$ Å, $c = 12.910(2)$ Å, $\beta = 101.30(2)°$, $V = 2733(1)$ Å$^3$, and $Z = 4$; **3c**·$C_7H_{14}$, triclinic, space group $P\bar{1}$ with $a = 12.849(4)$ Å, $b = 12.863(4)$ Å, $c = 12.610(7)$ Å, $\alpha = 110.61(3)°$, $\beta = 105.77(3)°$, $\gamma = 62.77(2)°$, $V = 1719(1)$ Å$^3$, and $Z = 2$; **4b**·$CH_2Cl_2$, triclinic, space group $P\bar{1}$ with $a = 12.647(3)$ Å, $b = 19.137(3)$ Å, $c = 12.550(2)$ Å, $\alpha = 105.765(11)°$, $\beta = 93.610(15)°$, $\gamma = 88.877(16)°$, $V = 2917.2(9)$ Å$^3$, and $Z = 2$; **4c**, orthorhombic, space group $Pba2$ with $a = 22.657(2)$ Å, $b = 10.570(2)$ Å, $c = 10.664(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2554(1)$ Å$^3$, and $Z = 2$; **6**, triclinic, space group $P\bar{1}$ with $a = 7.4667(8)$ Å, $b = 11.3406(12)$ Å, $c = 13.5470(14)$ Å, $\alpha = 108.000(2)°$, $\beta = 105.796(2)°$, $\gamma = 94.300(2)°$, $V = 1033.8(2)$ Å$^3$, and $Z = 2$.

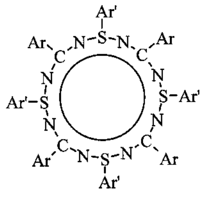
## Introduction

Inorganic polymers based on a backbone of p-block elements have a wide range of properties and applications.[1] Ring-opening polymerization (ROP) is a versatile method for generating such polymers, especially hybrid systems involving both PN and CN or SN units in the skeleton.[2,3] Ring strain considerations dictate the preference for six-membered cyclic precursors in ROP. Consequently, the polymers obtained involve an AAB (A = PN, B = CN, SN) sequence in the backbone. Polymers with alternating repeat units ABAB have been prepared by a condensation route.[4] Eight-membered ring systems of the type $A_2B_2$ or larger oligomers $A_nB_n$ ($n \geq 3$) represent an alternative potential source of such polymers.

Hybrid inorganic polymers containing CN and SN units have proved to be elusive. Recently, we described the ROP of the six-membered rings $Cl_3C_2N_3S$ and $Cl_3C_2N_3S(O)$ but, unlike the corresponding $P_2N_3S$ systems,[3] these polymerizations did not proceed cleanly owing to partial elimination of volatile sulfur chlorides during thermolysis.[5] Consequently, we turned our attention to eight-membered $(CNSN)_2$ rings. The S(IV) systems of type **1** and the related 16-membered rings **2** are obtained in reasonable yields by the reaction of trisilylated benzamidines with arene sulfenyl chlorides under kinetically controlled conditions.[6]



**1a**, Ar = 4-$BrC_6H_4$; Ar' = Ph
**1b**, Ar = 4-$CF_3C_6H_4$; Ar' = Ph
**1c**, Ar = 4-$CF_3C_6H_4$; Ar' = 4-$CH_3C_6H_4$



**2a**, Ar = 4-$BrC_6H_4$; Ar' = Ph
**2b**, Ar = 4-$CF_3C_6H_4$; Ar' = Ph
**2c**, Ar = 4-$CH_3C_6H_4$; Ar' = Ph
**2d**, Ar = 4-$CF_3C_6H_4$; Ar' = 4-$CH_3C_6H_4$

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(1) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.

(2) (a) Manners, I.; Allcock, H. R. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (b) Allcock, H. R.; Coley, S. M.; Manners, I.; Nuyken, O.; Renner, G. *Macromolecules* **1991**, *24*, 2024. (c) Allcock, H. R.; Coley, S. M.; Manners, I.; Visscher, K. B.; Parvez, M. *Inorg. Chem.* **1993**, *32*, 5088.

(3) (a) Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109. (b) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. (c) Liang, M.; Manners, I. *Makromol. Chem., Rapid Commun.* **1991**, 613. (d) Ni, Y.; Stammer, A.; Liang, M.; Massey, J.; Vancso, G. J.; Manners, I. *Macromolecules* **1992**, *25*, 7119. (e) Jaeger, R.; Lagowski, J. B.; Manners, I.; Vancso, G. J. *Macromolecules* **1995**, *28*, 9. (f) Allcock, H. R.; Dodge, J. A.; Manners, I. *Macromolecules* **1993**, *26*, 11.

(4) Chunechom, V.; Vidal, T. E.; Adams, H.; Turner, M. L. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1928.

(5) Chivers, T.; Gates, D.; Li, X.; Manners, I.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 70.

(6) Chivers, T.; Parvez, M.; Vargas-Baca, I.; Ziegler, T.; Zoricak, P. *Inorg. Chem.* **1997**, *36*, 1669.

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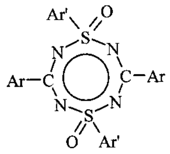
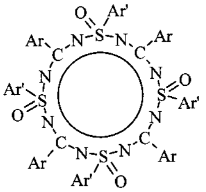
Upon photolysis or thermolysis the eight-membered S(IV) heterocycles undergo an unusual intramolecular isomerization to give the intensely colored diazenes Ar′SNC(Ar)N=NC(Ar)-NSAr′ rather than polymers of the type $[(Ar)CNS(Ar')N]_n$.[7] The corresponding 16-membered rings **2** are unaffected by photolysis. In this paper we describe the synthesis and X-ray structures of the 8- and 16-membered cyanuric−sulfanuric heterocycles **3a**−**c** and **4b**−**d**, respectively. We have also investigated the thermolysis and photolysis of **3b** and **3c** in order to determine whether the S(VI) systems undergo ROP, intramolecular isomerization, or an alternative process.





**3a**, Ar = 4-$BrC_6H_4$; Ar' = Ph
**3b**, Ar = 4-$CF_3C_6H_4$; Ar' = Ph
**3c**, Ar = 4-$CF_3C_6H_4$; Ar' = 4-$CH_3C_6H_4$

**4a**, Ar = 4-$BrC_6H_4$; Ar' = Ph
**4b**, Ar = 4-$CF_3C_6H_4$; Ar' = Ph
**4c**, Ar = 4-$CH_3C_6H_4$; Ar' = Ph
**4d**, Ar = 4-$CF_3C_6H_4$; Ar' = 4-$CH_3C_6H_4$

## Experimental Section

**Reagents and General Procedures.** All solvents used were distilled over appropriate drying agents and then stored over molecular sieves; solvents were dichloromethane ($P_2O_5$, $CaH_2$), pentane (Na), hexane (Na, benzophenone), diethyl ether (Na, benzophenone), THF (Na, benzophenone). The reagents 4-$XC_6H_4CN$ (X = Br, $CH_3$, $CF_3$), $Ph_2S_2$, and $Me_3SiCl$ were used as received from Aldrich. $SO_2Cl_2$ was received from Aldrich and distilled prior to use. Literature methods were used to prepare and purify the following reagents before use: *m*-chloroperbenzoic acid (*m*CPBA),[8] PhSCl,[9] and 4-$XC_6H_4CN_2(SiMe_3)_3$ (X = Br, $CH_3$, $CF_3$).[10] $LiN(SiMe_3)_2$ was obtained from Aldrich, and the monoetherate adduct was prepared by dissolving $LiN(SiMe_3)_2$ in hexanes and adding 1.1 equiv of diethyl ether. The adduct $LiN(SiMe_3)_2 \cdot Et_2O$ was then precipitated out of solution, washed with hexane, and stored in a drybox. The S(IV) heterocycles **1a**−**c**, **2b**, and **2d** were prepared by the reaction of a trisilylated benzamidine with 3 equiv of an arene sulfenyl chloride at very low temperatures, as reported in the literature.[6] The product mixtures were separated and purified by multiple recrystallizations in $CH_2Cl_2$/hexane and also by column chromatography using 170−250 Å mesh silica gel. The new 16-membered ring **2c** was obtained by a similar procedure and purified by fractional recrystallization from toluene. Anal. Calcd for $C_{56}H_{48}N_8S_4$: C, 69.97; H, 5.03; N, 11.66. Found: C, 69.98; H, 4.71; N, 11.44. EIMS: *m*/*z* = 961 ($M^+$, 100%).

**Instrumentation**. All $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker ACE 200 spectrometer or Varian XL-200 and analyzed by using Tecmag PowerMac 7300/180 software. All samples were run in deuterated solvents and referenced with respect to the residual protons. Chemical shifts are quoted relative to tetramethylsilane at 0 ppm. Infrared spectra were collected on a Mattson 4030 FT-IR spectrometer, and samples were prepared as Nujol mulls on KBr plates. Electron-impact mass spectra were obtained by using a VG 7070F micromass spectrometer operating at 70 eV. Elemental analyses were carried out by the Analytical Services Laboratory of the Chemistry Department at the University of Calgary.

The procedures for the syntheses of **3a**−**c**, **4a**−**c**, and **5** were very similar, and they are only reported in detail for **3a.** Reactions were carried out under an argon atmosphere with reaction vessels covered in aluminum foil to prevent photochemical decomposition of dithiatetrazocines. The products were manipulated in air and stored in sealed vials.

**Preparation of $(4\text{-}BrC_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (3a).** To a Schlenk vessel containing $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.100 g, 0.164 mmol) in 50 mL $CH_2Cl_2$ was added *m*CPBA (0.169 g, 0.983 mmol), also dissolved in 50 mL of $CH_2Cl_2$. The reaction mixture was stirred for 1 h at 23 °C. After removal of solvent, unreacted *m*CPBA and the byproduct *m*CBA were removed from the reaction mixture by several recrystallizations in a 2:1 pentane/$CH_2Cl_2$ mixture. In addition, it was sometimes necessary to perform an aqueous extraction with 10 equiv of $NaHCO_3$ to completely remove the carboxylic acids. The product **3a** was obtained as a colorless powder (0.077 g, 0.121 mmol, 74%). It was recrystallized from a mixture of $CH_2Cl_2$/pentane at −20 °C to yield colorless crystals of X-ray quality. Mp: 232 °C (turns red upon melting). Anal. Calcd for $C_{26}H_{18}N_4S_2O_2Br_2$: C, 48.76; H, 2.83; N, 8.75. Found: C, 48.26; H. 2.44; N, 8.62. $^1H$ NMR (in $CDCl_3$, $\delta$): 7.48 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H), 7.89 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H), 8.22 and 7.67 (m, $C_6H_5$, 5H). $^{13}C$ NMR (in $CDCl_3$, $\delta$): 167.31 (heterocyclic tertiary C), 143.74, 135.46, 132.91, 131.68, 131.57, 129.31, 128.73, 125.91. IR ($cm^{-1}$): 2726 (w), 1579 (m), 1547 (w), 1503 (m), 1332 (s), 1252 (m), 1184 (w), 1096 (w), 1064 (m), 1008 (m), 973 (w), 922 (w), 852 (m), 832 (m), 773 (m), 749 (w), 721 (w), 682 (m), 584 (m), 541 (w). EIMS: *m*/*z* = 642 ($M^+$).

**Preparation of $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (5).** To a Schlenk vessel containing $(4\text{-}BrC_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.116 g, 0.190 mmol) in 50 mL of THF was added *m*CPBA (0.197 g, 1.14 mmol) also dissolved in 50 mL of THF. The product **5** was obtained as a colorless powder (0.0907 g, 0.145 mmol, 76%). It was recrystallized from a mixture of $CH_2Cl_2$ and hexane at −20 °C to yield clear colorless crystals. X-ray quality crystals were obtained by slow evaporation of this solvent mixture at 23 °C. Mp: 221 °C (turns red upon melting). Anal. Calcd for $C_{26}H_{18}N_4S_2OBr_2$: C, 49.86; H, 2.90; N, 8.94. Found: C, 49.85; H, 2.81; N, 9.10. $^1H$ NMR (in $CDCl_3$, $\delta$): 8.33 (m, 1H), 8.19 (m, 1H), 7.98 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H), 7.69 (m, 3H), 7.48 (d, 4-$BrC_6(H_a)_2(H_b)_2$, 2H). $^{13}C$ NMR (in $CDCl_3$, $\delta$): 165.09 (heterocyclic tertiary C), 143.79, 143.65, 139.88, 136.70, 132.96, 132.48, 132.20, 131.74, 129.85, 129.12, 126.62, 125.98. IR ($cm^{-1}$): 2722 (w), 2674 (w), 2352 (w), 1579 (s), 1515 (s), 1311 (s), 1297 (m), 1284 (m), 1261 (w), 1194 (m), 1173 (m), 1157 (m), 1094 (m), 1066 (w), 1024 (w), 1004 (m), 969 (w), 922 (w), 844 (w), 809 (m), 723 (s), 681 (m), 626 (w), 576 (s). EIMS: *m*/*z* = 625 ($M^+$).

**Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (3b).** The heterocycle **3b** was obtained in 93% yield from the reaction of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(C_6H_5)_2$ (0.537 g, 0.912 mmol) and *m*CPBA (0.944 g, 5.47 mmol) in $CH_2Cl_2$ (100 mL). Colorless crystals of X-ray quality were grown by slow evaporation of $CH_2Cl_2$/hexane solution. Mp: 183 °C. Anal. Calcd for $C_{28}H_{18}N_4S_2O_2F_6$: C, 54.19; H, 2.93; N, 9.03. Found: C, 53.80; H. 2.86; N, 9.23. $^1H$ NMR (in $CDCl_3$, $\delta$): 8.15 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H), 8.23 and 7.52 (m, $C_6H_5$, 5H), 7.63 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H). $^{19}F$ NMR (in $CDCl_3$, $\delta$): −63.50. $^{13}C$ NMR (in $CDCl_3$, $\delta$): 166.79 (heterocyclic tertiary C), 143.26, 139.54, 132.97, 130.15, 129.23, 125.77, 125.26, 125.17. IR ($cm^{-1}$): 2360 (w), 2342 (w), 1593 (w), 1527 (s), 1356 (m), 1319 (s), 1248 (m), 1158 (m), 1134 (s), 1109 (s), 1067 (s), 1015 (m), 931 (w), 852 (m), 788 (m), 764 (m), 749 (m), 722 (w), 700 (w), 686 (w), 629 (w), 583 (m), 579 (m), 542 (w). EIMS: *m*/*z* = 620 ($M^+$).

**Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(4\text{-}CH_3C_6H_4)_2$ (3c).** The heterocycle **3c** was obtained in 98% yield by the reaction of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(4\text{-}CH_3C_6H_4)_2$ (0.345 g, 0.559 mmol) and *m*CPBA (0.579 g, 3.356 mmol) in $CH_2Cl_2$ (100 mL). Colorless crystals of X-ray quality were grown by slow evaporation of $CH_2Cl_2$/hexane solution. Mp: 187 °C (melts to yellow liquid). Anal. Calcd for $C_{30}H_{22}N_4S_2O_2F_6$: C, 55.55; H, 3.42; N, 8.64. Found: C, 55.16; H. 3.28; N, 7.84. $^1H$ NMR (in $CDCl_3$, $\delta$): 8.15 (d, 4-$CH_3C_6(H_c)_2(H_d)_2$, 2H), 8.11 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H), 7.61 (d, 4-$CH_3C_6(H_c)_2(H_d)_2$, 2H), 7.45 (d, 4-$CF_3C_6(H_a)_2(H_b)_2$, 2H), 2.53 (s, 4-$CH_3C_6H_4$, 3H). $^{13}C$ NMR (in $CDCl_3$, $\delta$): 166.52 (heterocyclic tertiary C), 143.87, 140.45, 139.69, 133.82,

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(7) Chivers, T.; Vargas-Baca, I.; Ziegler, T.; Zoricak, P. *Chem. Commun.* **1996**, 949.

(8) Traylor, T. G.; Lee, W. A.; Stynes, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 755.

(9) Mueller, W. H.; Butler, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2075.

(10) Boeré, R. T.; Oakley, R. T.; Reed, R. W. *J. Organomet. Chem.* **1987**, *331*, 161.

130.12, 129.79, 128.26, 125.82, 125.18, 125.10. IR (cm$^{-1}$): 1700 (w), 1592 (w), 1512 (m), 1349 (m), 1317 (s), 1263 (m), 1233 (w), 1190 (w), 1169 (m), 1130 (m), 1107 (m), 1065 (ms), 1016 (m), 925 (w), 845 (m), 806 (w), 782 (w), 758 (m), 721 (w), 695 (w), 654 (w). EIMS (M$^+$): $m/z = 649$ (M$^+$).

**Preparation of $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)(C_6H_5)_2$ (6).** A long Schlenk tube (20 cm long × 1 cm diameter) containing $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_5)_2$ (0.173 g, 0.279 mmol) was evacuated and placed in a furnace at 220 °C for 31 h. A black liquid melt formed at the bottom of the tube while white crystals of diphenylsulfide and a yellow liquid ($4\text{-}CF_3C_6H_4CN$) condensed at the cool end, which was outside the furnace. These volatile products were identified by comparison of their $^1$H NMR spectra with those of authentic samples. The black material was sublimed at 120 °C (0.01 mmHg) for 48 h to give a white sublimate (0.908 g, 0.203 mmol, 73%). Mp: 214−216 °C. Anal. Calcd for $C_{22}H_{13}N_3SOF_6$: C, 54.88; H, 2.72; N, 8.73; S, 6.65. Found: C, 55.00; H. 2.74; N, 8.73; S, 7.92. $^1$H NMR (in CDCl$_3$, $\delta$): 8.65 and 7.78 (d, $C_6H_4$, 8H), 7.92 (m, $C_6(H_a)_2(H_b)_3$, 2H), 7.66 (m, $C_6(H_a)_2(H_b)_3$, 3H). $^{13}$C NMR (in CDCl$_3$, $\delta$): 168.91 (heterocyclic tertiary C), 139.86, 138.84, 134.92, 134.34, 129.59, 129.28, 127.89, 125.43, 125.36. IR (cm$^{-1}$): 1695 (s), 1596 (w), 1574 (w), 1305 (m), 1263 (m), 1140 (w), 1099 (w), 1074 (w), 1027 (w), 917 (w), 897 (w), 849 (w), 808 (w), 750 (m), 720 (s), 667 (w), 652 (w), 545 (w). EIMS: $m/z = 481$ (M$^+$).

**Preparation of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (4b).** The heterocycle **4b** was obtained in 81% yield by the reaction of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (0.220 g, 0.187 mmol) and *m*CPBA (0.774 g, 4.49 mmol) in CHCl$_2$ (100 mL). The product was recrystallized from a mixture of CH$_2$Cl$_2$ and diethyl ether at −20 °C to yield clear colorless crystals. X-ray quality crystals were obtained by slow evaporation of a CH$_2$Cl$_2$/hexane solution at 23 °C. Mp: 226 °C (dec). Anal. Calcd for $C_{56}H_{36}N_8S_4O_4F_{12}$: C, 54.19; H, 2.93; N, 9.03. Found: C, 53.81; H. 2.80; N, 8.81. $^1$H NMR (in CDCl$_3$, $\delta$): 7.41 (m, $C_6(H_c)_2(H_d)_3$, 3H), 7.66 (m, $C_6(H_c)_2(H_d)_3$, 2H), 7.92 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 7.19 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H). $^{13}$C NMR (in CDCl$_3$, $\delta$): 170.85 (heterocyclic tertiary C), 141.84, 139.77, 133.51, 130.45, 129.20, 128.91, 126.83, 124.52 124.49. IR (cm$^{-1}$): 1655 (m), 1523 (w), 1504 (w), 1416 (s), 1317 (s), 1224 (m), 1172 (m), 1098 (m), 1018 (w), 1003 (w), 861 (m), 820 (m), 684 (w), 653 (m), 629 (w), 617 (w), 582 (w), 499 (w), 545 (w).

**Preparation of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4O_4(C_6H_5)_4$ (4c).** The heterocycle **4c** was obtained in 56% yield by the reaction of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4(C_6H_5)_4$ (0.181 g, 0.188 mmol) and *m*CPBA (0.780 g, 4.52 mmol) in CHCl$_2$ (100 mL). The product was recrystallized from a mixture of CH$_2$Cl$_2$ and hexane at −20 °C to yield clear colorless crystals. X-ray quality crystals were obtained by slow evaporation of a CH$_2$Cl$_2$/hexane solution at 23 °C. Mp: 202 °C (dec). Anal. Calcd for $C_{56}H_{48}N_8S_4O_4\cdot CH_2Cl_2$: C, 61.72; H, 4.55; N, 10.11. Found: C, 62.13; H, 4.47; N, 10.14. $^1$H NMR (in CDCl$_3$, $\delta$): 7.49 (m, $C_6(H_c)_2(H_d)_3$, 3H), 7.30 (m, $C_6(H_c)_2(H_d)_3$, 2H), 7.89 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 6.81 (d, $4\text{-}CH_3C_6(H_a)_2(H_b)_2$, 2H), 2.22 (s, $4\text{-}CH_3C_6H_5$, 3H). $^{13}$C NMR (in CDCl$_3$, $\delta$): 170.44 (heterocyclic tertiary C), 142.45, 140.29, 133.96, 133.69, 132.28, 129.35, 129.02, 128.65, 128.50. IR (cm$^{-1}$): 1654 (m), 1560 (m), 1489 (m), 1398 (m), 1309 (w), 1227 (m), 1172 (w), 1111 (m), 1095 (s), 1022 (w), 948 (w), 851 (s), 807 (w), 791 (w), 748 (m), 727 (m), 689 (w), 661 (w), 591 (s), 510 (w). FAB-MS (M$^+$): $m/z = 1025$.

**Preparation of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4O_4(4\text{-}CH_3C_6H_4)_4$ (4d).** The heterocycle **4d** was obtained in 76% yield by the reaction of $(4\text{-}CF_3C_6H_4)_4C_4N_8S_4(4\text{-}CH_3C_6H_4)_4$ (0.161 g, 0.131 mmol) with *m*CPBA (0.361 g, 2.10 mmol) in CH$_2$Cl$_2$ (100 mL). The product was recrystallized from a mixture of CH$_2$Cl$_2$ and diethyl ether at −20 °C to yield clear colorless crystals. X-ray quality crystals were obtained by slow evaporation of a CH$_2$Cl$_2$/hexane solution at 23 °C. Mp: >270 °C. Anal. Calcd for $C_{60}H_{44}N_8S_4O_4F_{12}$: C, 55.55; H, 3.42; N, 8.64. Found: C, 55.45; H, 3.86; N, 8.99. $^1$H NMR (in CDCl$_3$, $\delta$): 7.75 and 7.17 (d, $4\text{-}CF_3C_6H_4$, 2H), 7.65 and 7.14 (d, $4\text{-}CH_3C_6H_4$, 2H), 2.42 (s, $4\text{-}CH_3C_6H_5$, 3H). $^{13}$C NMR (in CDCl$_3$, $\delta$): 170.89 (heterocyclic tertiary C), 144.53, 139.88, 138.96, 130.44, 129.72, 128.96, 126.85, 125.32, 124.41, 124.38. IR (cm$^{-1}$): 1597 (m), 1575 (m), 1522 (m), 1506 (m), 1418 (s), 1322 (s), 1221 (s), 1125 (s), 1097 (s), 1018 (m), 951 (m), 901 (w), 857 (s), 821 (s), 777 (w), 639 (m), 625 (m), 601 (m), 578 (w), 512 (m), 461 (m).

**Table 1.** Crystallographic Data for **3b**, **3c**·C$_7$H$_{16}$, and **6**

| | **3b** | **3c**·C$_7$H$_{16}$ | **6** |
|---|---|---|---|
| formula | $C_{28}H_{18}N_4F_6S_2O_2$ | $C_{30}H_{22}N_4F_6S_2O_2\cdot C_7H_{16}$ | $C_{12}H_{13}N_3F_6OS$ |
| fw | 620.59 | 748.84 | 481.41 |
| cryst syst | monoclinic | triclinic | triclinic |
| space group | $P2_1/a$ (no. 14) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| *a*, Å | 7.316(2) | 12.849(4) | 7.4667(8) |
| *b*, Å | 29.508(5) | 12.863(4) | 11.3406(12) |
| *c*, Å | 12.910(2) | 12.610(7) | 13.5470(14) |
| α, deg | 90 | 110.61(3) | 108.000(2) |
| $\beta$, deg | 101.30(2) | 105.77(3) | 105.796(2) |
| $\gamma$, deg | 90 | 62.77(2) | 94.300(2) |
| *V*, Å$^3$ | 2733(1) | 1719(1) | 1033.8(2) |
| *Z* | 4 | 2 | 2 |
| $d_{calc}$, g cm$^{-3}$ | 1.508 | 1.447 | 1.547 |
| *T*, °C | 23.0 | −103.0 | −80.0 |
| $\mu$, cm$^{-1}$ | 2.59 | 2.29 | 2.31 |
| $R^a$ | 0.0855 | 0.0692 | 0.0523 |
| $R_w$ $^b$ | 0.250 | 0.1937 | 0.1293$^c$ |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ [$I > 2.00\sigma(I)$ and $I > 3.00\sigma(I)$]. [b] $R_w = \{[\sum w(F_o - F_c)^2]/[\sum wF_o^2]\}^{1/2}$. [c] $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$ (all data).

**Table 2.** Crystallographic Data for **2c**, **4b**·CH$_2$Cl$_2$, and **4c**

| | **2c** | **4b**·CH$_2$Cl$_2$ | **4c** |
|---|---|---|---|
| formula | $C_{56}H_{48}N_8S_4$ | $C_{56}H_{36}N_8S_4O_4F_{12}\cdot CH_2Cl_2$ | $C_{56}H_{48}N_8S_4O_4$ |
| fw | 961.29 | 1326.11 | 1025.29 |
| cryst syst | triclinic | triclinic | orthorhombic |
| space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) | *Pba*2 (no. 32) |
| *a*, Å | 13.917(2) | 12.647(3) | 22.657(2) |
| *b*, Å | 15.610(4) | 19.137(3) | 10.570(2) |
| *c*, Å | 13.491(3) | 12.550(2) | 10.664(3) |
| α, deg | 95.77(2) | 105.765(11) | 90 |
| $\beta$, deg | 114.82(1) | 93.610(15) | 90 |
| $\gamma$, deg | 76.21(2) | 88.877(16) | 90 |
| *V*, Å$^3$ | 2583(1) | 2917.2(9) | 2554(1) |
| *Z* | 2 | 2 | 2 |
| $d_{calc}$, g cm$^{-3}$ | 1.236 | 1.510 | 1.333 |
| *T*, °C | −103.0 | −103.0 | −103.0 |
| $\mu$, cm$^{-1}$ | 2.29 | 3.47 | 2.42 |
| $R^a$ | 0.049 | 0.067 | 0.0562 |
| $R_w$ $^b$ | 0.030 | 0.058 | 0.156 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(F_o - F_c)^2]/\sum[wF_o^2]\}^{1/2}$.

**X-ray Analyses.** All measurements for **2c**, **3b**, **3c**·C$_7$H$_{14}$, **4b**·CH$_2$Cl$_2$, and **4c** were made on a Rigaku AFC6S diffractometer. The measurements for **6** were carried out on a Bruker AXS SMART 1000 CCD diffractometer. Crystallographic data are summarized in Tables 1 and 2.

**(a) 3b.** A colorless block of **3b** (0.35 mm × 0.25 mm × 0.18 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $15.0° < 2\theta < 25.0°$. Scans of $(0.73 + 0.34 \tan\theta)°$ were made at a speed of 8.0 deg/min$^{-1}$ to a maximum $2\theta$ value of 50.1°. The intensities of 4939 unique reflections were measured, of which 1615 had $I > 2.00\sigma(I)$. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods[11] and expanded using Fourier techniques.[12] The non-hydrogen atoms were refined anisotropically. The CF$_3$ groups were disordered and were included over two sites, each with partial occupancy factors. Hydrogen atoms were included but not refined. For all six structures,

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[11] SIR92. Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

scattering factors were those of Cromer and Waber[13] and allowance was made for anomalous dispersion.[14] All calculations were performed using teXsan.[15]

**(b) 3c·$C_7H_{16}$.** A colorless prismatic crystal of **3c**·$C_7H_{16}$ (0.50 mm × 0.40 mm × 0.37 mm) was mounted on a glass fiber and coated with epoxy glue. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.22° < 2\theta < 21.47°$. Scans of $(1.57 + 0.34 \tan \theta)°$ were made at a speed of 4.0 deg/min$^{-1}$. The intensities of 7930 reflections were measured, of which 4412 had $I > 2.00\sigma(I)$. The solution and refinement of the structure followed the procedures described above for **3b**. The carbon atoms for the $C_7H_{12}$ molecule were disordered and were allowed to refine with isotropic thermal parameters over 12 sites with partial occupancy factors.

**(c) 4b·$CH_2Cl_2$.** A colorless plate of **4b**·$CH_2Cl_2$ (0.50 mm × 0.32 mm × 0.09 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $18.51° < 2\theta < 23.18°$. Scans of $(1.52 + 0.34 \tan \theta)°$ were made at a speed of 8.0 deg/min$^{-1}$. The intensities of 13 491 reflections were measured, of which 3383 had $I > 3.00\sigma(I)$. The solution and refinement of the structure followed the procedures described above for **3b**.

**(d) 4c.** A colorless plate of **4c** (0.60 mm × 0.40 mm × 0.20 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $15.0° < 2\theta < 25.0°$. Scans of $(1.47 + 0.34 \tan \theta)°$ were made at a speed of 4.0 deg/min$^{-1}$. The intensities of 3112 reflections were measured, of which 1621 had $I > 2.00\sigma(I)$. The solution of the structure followed the procedures described above for **3b**, and the refinement was carried out with the aid of SHELXL-97.[16a]

**(e) 2c.** A colorless plate of **2c** (0.53 mm × 0.17 mm × 0.12 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $13.72° < 2\theta < 19.65°$. Scans of $(1.15 + 0.34 \tan \theta)°$ were made at a speed of 4.0 deg/min$^{-1}$. The intensities of 9150 reflections were measured, of which 3316 had $I > 3.00\sigma(I)$. The structure was solvent by direct methods,[17] and refinement followed the procedures described for **3b**.

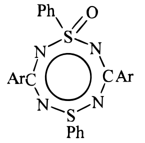
**(f) 6.** Suitable crystals of **6** were obtained by sublimation at 120 °C/10$^{-2}$ Torr. A colorless plate of **6** (0.45 mm × 0.05 mm × 0.05 mm) was coated with oil (Paratone 8277, Exxon) and mounted on a glass fiber. A total of 5129 reflections were collected, of which 2309 had $I > 2.00\sigma(I)$. The structure was solved by direct methods,[16a] and refined by full-matrix least-squares methods on $F^2$ with SHELX97-2.[16b] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined.

## Results and Discussion

**Synthesis and Spectroscopic Characterization of 3a−c and $(4\text{-}BrC_6H_4)_2C_2N_4S(Ph)S(O)Ph$ (5).** In a previous investigation we showed that *m*CPBA is the preferred oxidizing agent for the conversion of $P_2N_4S(IV)_2$ rings to the corresponding phosphazene−sulfanuric systems.[18] In a similar way the eight-membered cyanuric−sulfanuric ring systems **3a−c** were obtained in excellent yields (74−98%) by the reaction of the corresponding dithiatetrazocines **1a−c** with an excess of *m*CPBA in $CH_2Cl_2$ at 23 °C. In the early stages of this investigation the byproduct *m*-chlorobenzoic acid and unreacted *m*CPBA were removed from the product mixture by treatment with aqueous $KHCO_3$ solution and subsequent recrystallization from pentane− or hexane−$CH_2Cl_2$ mixtures. Subsequently, it was found that treatment of a $CH_2Cl_2$ solution of the crude product with $NH_3$ gas is a more efficient way of removing these carboxylic acids (as insoluble $NH_4^+$ salts).[19] These new heterocycles are air-stable white solids that were shown to decompose via ring contraction above 200 °C (vide infra). Oakley et al. have isolated the related ring system $(Me_2N)_2C_2N_4S_2(O)_2[N(CF_3)_2]_2$ in 26% yield from the reaction in $(Me_2N)_2C_2N_4S_2$ with the nucleophilic radical $(CF_3)_2NO$.[20]

The derivatives **3a−c** were characterized by elemental analyses, EIMS, IR, and $^1H/^{13}C$ NMR spectra. The $C_2N_4S_2$ ring conformation in **3b** and **3c** was established by X-ray crystallography. All three derivatives give rise to strong molecular ions in the EI mass spectrum. The $^1H$ NMR spectra of **3a** and **3b** exhibit two doublets in the aromatic region, characteristic of the $A_2B_2$ pattern for 4-$XC_6H_4$ groups (X = Br, $CF_3$) attached to carbon, in addition to the multiplet resonance for the $C_6H_5$ groups attached to sulfur. In the case of **3c** there are two sets of two doublets corresponding to the 4-$CF_3C_6H_4$ and 4-$CH_3C_6H_4$ groups attached to C and S, respectively. The $^{13}C$ NMR spectra of **3a−c** exhibit a characteristic resonance for the heterocyclic carbon atoms at $\delta$ 165−167, which is shifted only slightly (ca. 1 ppm) compared to the corresponding resonance for the S(IV) systems **1a−c**. The IR spectra of **3a−c** exhibit a characteristic band at ca. 1310 cm$^{-1}$ attributed to $\nu$(S=O).

The oxidation of **1a** by *m*CPBA proceeds more slowly in THF than in $CH_2Cl_2$, and the monoxide $(4\text{-}BrC_6H_4)_2C_2N_4S_2O(C_6H_5)_2$ (**5**) was isolated in 76% yield when THF was used as the solvent. The mixed oxidation state [S(IV) and S(VI)] heterocycle **5** exhibited a strong molecular ion in the EI mass spectrum and a band at 1311 cm$^{-1}$ in the IR spectrum assigned to $\nu$(S=O). The $^1H$ NMR spectrum of **5** differs from that of the corresponding dioxide **3a** in the appearance of two multiplets for the different $C_6H_5$ groups attached to S(IV) and S(VI), respectively, in addition to the $A_2B_2$ pattern for the equivalent 4-$BrC_6H_4$ groups. The X-ray structure of **5** was determined.[21]



**5**, (Ar = 4-$BrC_6H_4$)

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(12) DIRDIF94. Beuskens, P. T.; Admiraal, G.; Beuskens, G.; Bosman, W. P.; Garcia-Granda, R. S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(13) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71−98, Table 2.2A.

(14) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(15) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985, 1992.

(16) (a) Sheldrick, G. M. *SHELX97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELX97-2, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(17) Fan, Hai-Fu. *SAPI91, Structure Analysis Program with Intelligent Control*; Rigaku Corp.: Tokyo, 1991.

(18) Brock, M.; Chivers, T.; Parvez, M. *Inorg. Chem.* **1998**, *37*, 3263.

(19) Kondo, K.; Negishi, A. *Tetrahedron* **1971**, *27*, 4821.

(20) Boeré, R. T.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 868.

(21) Crystal data for **5** at −103 °C: $C_{26}H_{18}N_4S_2OBr_2$, $M$ = 626.38, orthorhombic, space group *Pbcn*, $a = 12.246(5)$ Å, $b = 7.818(4)$ Å, $c = 25.402(8)$ Å, $V = 2431(1)$ Å$^3$, and $Z = 4$. Of the 1747 reflections, 456 had $I > 3.00\sigma(I)$. The structure was solved by direct methods (SAPI91) and refined by Fourier techniques (DIRDIF94). The non-hydrogen atoms were refined anisotropically with the exception of the carbon atom in the heterocyclic ring, which was refined isotropically. The oxygen atom was required by the space group symmetry to be disordered and was allowed an occupancy factor of 0.5. The final $R$ and $R_w$ values were 0.0438 and 0.0434, respectively.

However, the oxygen atom in this structure was disordered with ca. 50% occupancy factors on each sulfur atom. Consequently, a detailed discussion of the structural parameters is not warranted. We note, however, that the X-ray analysis did confirm that **5** is the proposed mixed oxidation state system and that the $C_2N_4S_2$ ring retains a boat conformation.

**Synthesis and Spectroscopic Characterization of 4b−d.** The 16-membered cyanuric−sulfanuric ring systems **4b**−**d** were prepared in 55−80% yields by the oxidation of the corresponding S(IV) systems **2b**−**d** with an excess of *m*CPBA in $CH_2Cl_2$ at 23 °C. These new $C_4N_8S_4$ heterocycles are air-stable white solids that can be stored in screw-top vials for >6 months without degradation. They were characterized by CHN analyses, mass spectra, and IR and $^1H/^{13}C$ NMR spectra. The structures of **4b** and **4c** were determined by X-ray crystallography. Although molecular ions were not observed in the EI mass spectra of the 16-membered rings, the derivative **4c** exhibited a molecular ion in the FAB mass spectrum. A strong band at 1310−1320 $cm^{-1}$ in the IR spectra of **4b**−**d** is attributed to $\nu(S{=}O)$. The $^{13}C$ NMR spectra of all three derivatives revealed a singlet at ca. $\delta$ 171 for the heterocyclic carbon atom, which is shifted approximately 10 ppm upfield compared to the corresponding resonance for the S(IV) analogues **2b**−**d**.

The formation of intermediate S(IV)/S(VI) 16-membered ring systems from the oxidation of **2c** was monitored by $^1H$ NMR spectroscopy using the resonance of the 4-$CH_3C_6H_4$ group at ca. $\delta$ 2.2 as the NMR probe. Aliquots of *m*CPBA were added to a solution of **2c** in $CDCl_3$ 4 equiv at a time, and the $^1H$ NMR spectrum was recorded after mixing the reagents for 20 min. After the addition of 4 equiv of *m*CPBA three major resonances were observed at $\delta$ 2.21, 2.25, and 2.31. The former resonance corresponds to the S(VI) system **4c**, while the middle peak is attributed to the S(IV) ring **2c**. Thus, the resonance at $\delta$ 2.31 can be assigned to a mixed S(IV)/S(VI) ring system. Since this major intermediate gives rise to a singlet, it must have a single environment for the four $C\mathit{H}_3C_6H_4$ groups. We propose, therefore, that it is the dioxide $(4\text{-}CH_3C_6H_4)_4C_4N_8(SPh)[S(O)Ph]_2$ in which the oxygens are attached to antipodal sulfur atoms. Upon addition of a further 4 equiv of *m*CPBA to the reaction mixture, the resonance for this intermediate increases in intensity at the expense of the resonance for **2c**. Attempts to separate the major intermediate from **2c** and **4c** by TLC or column chromatography on silica gel were unsuccessful because of their similar elution times. Finally, the addition of 12 more equivalents of *m*CPBA produced a dominant singlet at $\delta$ 2.21 consistent with complete oxidation to **4c**.

**X-ray Structures of 3b and 3c·$C_7H_{16}$.** ORTEP drawings of **3b** and **3c**·$C_7H_{16}$ are shown in Figure 1. The $C_2N_4S_2$ ring retains a boat conformation upon oxidation (cf. $(Me_2N)_2C_2N_4S_2(O)_2[N(CF_3)_2]_2$).[20] However, the boat is twisted compared to the $C_2N_4S_2$ ring in the corresponding S(IV) systems **1a** and **1b**,[6] apparently in order to minimize steric interactions between the endo oxygen substituents attached to the sulfur atoms. A quantitative indication of the distortion of the boat conformation is provided by the comparison of the SNCN and NSNC torsion angles for **1b**, **3b**, and **3c** given in Table 3, from which it can be seen that the distortions in **3b** and **3c** are quite disparate. A second difference between the structures of **3b** and **3c**·$C_7H_4$, which is illustrated in Figure 1, concerns the relative orientations of the aryl rings attached to sulfur. In **3b** the $C_6H_5$ groups attached to S(1) and S(2) are at approximately 90° to each other, whereas the 4-$CH_3C_6H_4$ groups in **3c**·$C_7H_{14}$ are parallel to each other.

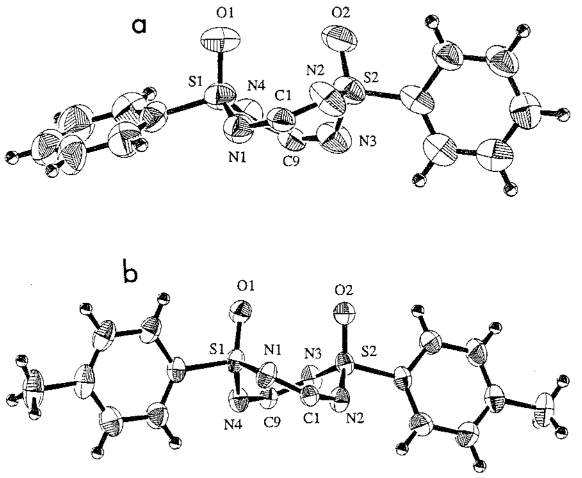


**Figure 1.** ORTEP diagrams of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2(O)_2(C_6H_4X\text{-}4)_2$: (a) X = H, **3b**; (b) X = $CH_3$, **3c**. The 4-$CF_3C_6H_4$ groups attached to carbon are omitted for clarity.

**Table 3.** Selected Torsion Angles (deg) for **1b**, **3b**, and **3c**·$C_7H_{14}$

| | **1b** | **3b** | **3c**·$C_7H_{14}$ |
|---|---|---|---|
| S(1)−N(4)−C(9)−N(3) | −17(1) | −18.5(17) | 31.6(5) |
| S(1)−N(1)−C(1)−N(2) | 6(1) | −31.7(18) | 16.0(6) |
| S(2)−N(3)−C(9)−N(4) | 3(1) | −33.6(15) | 16.0(6) |
| S(2)−N(2)−C(1)−N(1) | −15(1) | 13.4(14) | 29.0(6) |
| N(4)−S(1)−N(1)−C(1) | −78.6(6) | 89.7(11) | 38.8(4) |
| N(3)−S(2)−N(2)−C(1) | 82.4(6) | −38.9(13) | −93.6(4) |
| N(2)−S(2)−N(3)−C(9) | −66.2(7) | 98.1(10) | 35.8(4) |
| N(1)−S(1)−N(4)−C(9) | 93.3(6) | −29.3(13) | −94.7(3) |

**Table 4.** Selected Bond Lengths (Å) and Bond Angles (deg) for **3b** and **3c**·$C_7H_{18}$

Bond Length

| | **3b** | **3c**·$C_7H_{18}$ |
|---|---|---|
| S(1)−N(4) | 1.601(10) | 1.584(3) |
| S(1)−N(1) | 1.565(10) | 1.599(3) |
| S(2)−N(3) | 1.595(10) | 1.605(3) |
| S(2)−N(2) | 1.596(10) | 1.579(3) |
| N(3)−C(9) | 1.368(13) | 1.329(5) |
| N(4)−C(9) | 1.312(13) | 1.348(4) |
| N(1)−C(1) | 1.334(13) | 1.326(5) |
| N(2)−C(1) | 1.309(14) | 1.343(5) |
| S(1)−O(1) | 1.434(8) | 1.434(3) |
| S(2)−O(2) | 1.412(9) | 1.432(3) |
| C(1)−C(2) | 1.512(12) | 1.494(4) |
| S(1)−C(17) | 1.763(8) | 1.743(2) |
| C(9)−C(10) | 1.438(9) | 1.475(3) |
| S(2)−C(23) | 1.724(7) | 1.752(2) |

Bond Angle

| | **3b** | **3c**·$C_7H_{18}$ |
|---|---|---|
| N(4)−S(1)−N(1) | 113.8(5) | 112.2(2) |
| N(3)−S(2)−N(2) | 112.4(5) | 112.8(2) |
| S(1)−N(4)−C(9) | 129.0(7) | 125.9(3) |
| S(2)−N(3)−C(9) | 126.1(8) | 124.0(2) |
| S(2)−N(2)−C(1) | 124.3(8) | 127.1(3) |
| S(1)−N(1)−C(1) | 127.8(8) | 122.4(3) |
| N(4)−C(9)−N(3) | 124.6(8) | 128.8(3) |
| N(2)−C(1)−N(1 | 130.1(11) | 130.3(4) |
| C(17)−S(1)−O(1) | 108.4(5) | 109.1(2) |
| C(23)−S(2)−O(2) | 110.9(5) | 108.4(2) |

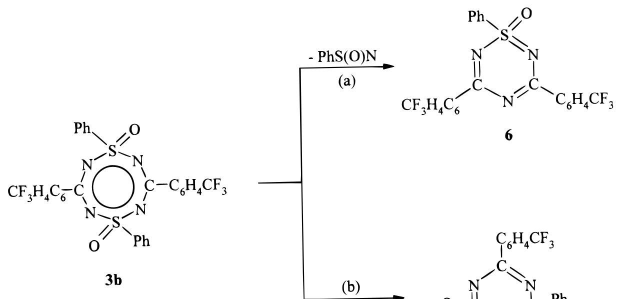
The bond distances and bond angles involving the $C_2N_4S_2$ rings in **3b** and **3c**·$C_7H_{14}$ are summarized in Table 4. The pertinent structural parameters for the S(VI) heterocycles are compared with those of the corresponding S(IV) system **1b** in Table 5. The mean S−N bond distance is shortened by ca. 0.05 Å upon oxidation, whereas *d*(CN) is unaffected. Similar observations have been reported for the analogous $P_2N_4S_2$

**Table 5.** Comparison of Structural Parameters for **1b**, **3b**, and **3c**·$C_7H_{14}$[a]

| | **1b** | **3b** | **3c**·$C_7H_{14}$ |
|---|---|---|---|
| *d*(S−N) | 1.623(5)−1.652(5) | 1.565(10)−1.601(10) | 1.579(3)−1.605(3) |
| \|*d*(S−N)\| | 1.640 | 1.589 | 1.592 |
| *d*(C−N) | 1.312(7)−1.348(7) | 1.309(14)−1.368(13) | 1.326(5)−1.348(4) |
| \|*d*(C−N)\| | 1.327 | 1.331 | 1.336 |
| ∠SNC | 118.1(5)−125.5(5) | 124.3(8)−129.0(7) | 122.4(3)−127.1(3) |
| \|∠SNC\| | 121.6 | 126.8 | 124.8 |
| \|∠NSN\| | 113.3 | 113.1 | 112.5 |

[a] Bond lengths in Å; bond angles in deg.

### Scheme 1



systems.[18] The bond angles ∠SNC are enlarged by ca. 5° upon oxidation while ∠NSN does not change significantly. The SO bond distances of 1.412(9)−1.434(8) Å in **3b** and **3c**·$C_7H_{14}$ are in the expected range for $S^{VI}{=}O$ double bonds [cf. *d*(SO) = 1.417(3) Å in 1,5-$(Me_2N)_2C_2N_4[S(O)N(CF_3)_2]_2$[20] and 1.438(3)−1.448(3) Å in *trans*-$Ph_4P_2N_4[S(O)Ph]_2$].[18]

**Thermolysis and Photolysis of $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2O_2(C_6H_5)_2$ (3b).** The thermolysis of **3b** was investigated as a possible route to cyanuric−sulfanuric polymers via ring-opening polymerization. The thermal decomposition of **3b** at 220 °C for 31 h produced the six-membered ring $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)Ph$ (**6**) in 71% yield (Scheme 1). The cyanuric−sulfanuric heterocyle was identified by CHNS analyses, mass spectrometry, $^1H/^{13}C$ NMR spectra, and X-ray crystallography. The EI mass spectrum exhibited a parent ion at *m*/*z* 481. The $^1H$ NMR spectrum of **6** exhibited the typical $A_2B_2$ pattern for 4-$CF_3C_6H_4$ groups attached to C and a multiplet for the $C_6H_5$ groups in the integrated ratio 8:5 consistent with the loss of a sulfanuric group NS(O)Ph from **3b** upon thermolysis. This inference was confirmed by an X-ray structural determination of **6** (see Figure 2). Pertinent bond lengths and bond angles are summarized in Table 6. The sulfur atom in this six-membered ring is ca. 0.26 Å out of the $C_2N_3S$ plane. The geometry at the carbon atoms C(1) and C(2) is exactly planar. The other structural parameters are similar to those found for the other cyanuric−sulfanuric ring systems in this work.

As indicated in Scheme 1, the ring contraction of **3b** may occur either (a) by loss of a sulfanuric group PhS(O)N or (b) by the elimination of 4-$CF_3C_6H_4C{\equiv}N$. $^1H$ NMR analysis of the volatile products of the thermal decomposition identified $Ph_2S_2$ as the major component with smaller amounts of 4-$CF_3C_6H_4$-CN. Thus, pathway a represents the major decomposition route for **3b**, although pathway b occurs to some extent. The formation of $Ph_2S_2$ from the eliminated PhS(O)N fragment is puzzling. We note, however, that Maricich observed the formation of $Ph_2S_2$ as a byproduct in the synthesis of $[NS(O)Ph]_3$ from PhS(O)Cl and $NaN_3$, which presumably occurs via decomposition of $PhS(O)N_3$ into "PhS(O)N".[22] Ring contraction has been observed for other eight-membered S−N ring systems (e.g., 1,3-$(Me_2NCN)_2(NSCl)_2$ loses $Me_2NCN$ to form $(Me_2NCN)(NSCl)_2$,[23] and 1,3-$(Ph_2PN)_2(NSCl)_2$ loses a NSCl unit to form the six-membered ring $(Ph_2PN)_2(NSCl)$).[24]

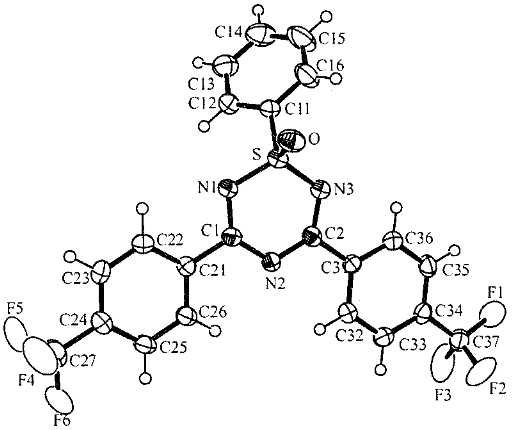


**Figure 2.** ORTEP drawing of $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)Ph$ (**6**).

**Table 6.** Selected Bond Lengths (Å) and Bond Angles (deg) for **6**

| | | | |
|---|---|---|---|
| S−O | 1.434(2) | O−S−N(1) | 113.67(13) |
| S−N(1) | 1.584(2) | O−S−N(3) | 111.89(12) |
| S−N(3) | 1.599(3) | N(1)−S−N(3) | 110.57(13) |
| S−C(11) | 1.750(3) | O−S−C(11) | 108.74(13) |
| | | N(1)−S−C(11) | 106.46(13) |
| N(1)−C(1) | 1.339(4) | N(3)−S−C(11) | 104.97(13) |
| N(2)−C(1) | 1.345(3) | C(1)−N(1)−S | 116.36(19) |
| N(2)−C(2) | 1.345(3) | C(1)−N(2)−C(2) | 117.8(3) |
| N(3)−C(2) | 1.333(4) | C(2)−N(3)−S | 116.6(2) |
| C(1)−C(21) | 1.482(4) | N(1)−C(1)−N(2) | 127.6(3) |
| C(2)−C(31) | 1.484(4) | | |
| | | N(1)−C(1)−C(21) | 115.9(2) |
| | | N(2)−C(1)−C(21) | 116.4(3) |
| | | N(3)−C(2)−C(2) | 127.9(3) |
| | | N(3)−C(2)−C(31) | 116.1(2) |
| | | N(2)−C(2)−C(31) | 116.0(3) |

The observed preference for pathway a in the decomposition of **3b** is not easily explained, since the formation of a $-C{\equiv}N$ triple bond will provide a strong driving force for pathway b. The eight-membered ring **3c** undergoes a similar ring contraction process at ca. 220 °C to give $(4\text{-}CF_3C_6H_4)_2C_2N_3S(O)(C_6H_4CH_3\text{-}4)$, which was identified by observation of the molecular ion in the EI mass spectrum.

The photolysis of **3b** at 25 °C in toluene was also investigated for comparison with the behavior upon thermolysis. The photolysis was conducted in a quartz UV cell using 254 nm radiation, and the formation of products was monitored by $^1H$ NMR at regular intervals over a 20 h period. The formation of the six-membered ring **6** was readily evident from the appearance of the characteristic doublet centered at $\delta$ 8.65. The intensity of this resonance reached a maximum after ca. 6 h and then decreased. After 20 h the $^{19}F$ NMR spectrum of the toluene solution revealed two strong and two medium intensity resonances in the region $\delta$ −63.0 to −63.4, indicating the formation of a complex mixture of products. From the NMR data it can be concluded that photolysis also engenders ring contraction, but the thermolysis of **3b** provides a cleaner route to **6**.

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(22) Maricich, T. J. *J. Am. Chem. Soc.* **1968**, *90*, 7179.
(23) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 47.
(24) Burford, N.; Chivers, T.; Rao, N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

**Table 7.** Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **2c**, **4b**, and **4c**

| **2c** | | **4c** | | **4b** | |
|---|---|---|---|---|---|
| S(1)−N(1) | 1.659(5) | S(2)−N(3) | 1.597(7) | S(2)−N(3) | 1.610(9) |
| S(1)−C(5) | 1.797(7) | S(2)−N(4) | 1.596(7) | S(2)−N(2) | 1.561(9) |
| S(2)−N(3) | 1.668(5) | S(1)−N(1) | 1.577(6) | S(1)−N(1) | 1.623(10) |
| S(3)−N(4) | 1.660(5) | S(1)−N(2) | 1.611(7) | S(1)−N(8) | 1.571(9) |
| S(3)−C(17) | 1.786(7) | N(3)−C(15) | 1.326(10) | S(4)−N(7) | 1.622(9) |
| S(4)−N(7) | 1.684(5) | N(2)−C(15) | 1.325(8) | S(4)−N(6) | 1.603(10) |
| N(1)−C(1) | 1.331(8) | N(4*)−C(1) | 1.366(10) | S(3)−N(4) | 1.599(9) |
| N(3)−C(2) | 1.334(8) | N(1*)−C(1) | 1.311(10) | S(3)−N(5) | 1.616(10) |
| N(5)−C(3) | 1.326(8) | S(2)−O(2) | 1.433(6) | N(2)−C(3) | 1.326(13) |
| N(7)−C(4) | 1.328(7) | S(1)−O(1) | 1.444(6) | N(4)−C(2) | 1.336(13) |
| S(1)−N(8) | 1.644(5) | | | N(5)−C(3) | 1.310(14) |
| S(2)−N(2) | 1.659(5) | | | N(6)−C(3) | 1.314(13) |
| S(2)−C(11) | 1.801(7) | | | N(7)−C(4) | 1.352(14) |
| S(3)−N(5) | 1.693(5) | | | N(8)−C(4) | 1.326(13) |
| S(4)−N(6) | 1.644(5) | | | N(1)−C(1) | 1.344(14) |
| S(4)−C(23) | 1.800(7) | | | N(2)−C(1) | 1.331(13) |
| N(2)−C(1) | 1.352(7) | | | S(1)−O(1) | 1.443(8) |
| N(4)−C(2) | 1.335(7) | | | S(2)−O(2) | 1.443(8) |
| N(6)−C(3) | 1.332(7) | | | S(3)−O(3) | 1.451(8) |
| N(8)−C(4) | 1.317(7) | | | S(4)−O(4) | 1.445(8) |
| N(1)−S(1)−N(8) | 107.3(3) | N(2)−S(1)−N(1) | 105.2(4) | N(5)−S(3)−N(4) | 109.0(5) |
| N(8)−S(1)−C(5) | 100.5(3) | N(4)−S(2)−N(3) | 105.1(4) | N(3)−S(2)−N(2) | 112.2(5) |
| N(2)−S(2)−C(11) | 100.9(3) | S(1)−N(2)−C(15) | 116.1(6) | N(1)−S(1)−N(8) | 106.7(5) |
| N(4)−S(3)−N(5) | 106.5(3) | S(2)−N(3)−C(15) | 127.4(5) | N(7)−S(4)−N(6) | 106.2(5) |
| N(5)−S(3)−C(17) | 97.5(3) | S(2)−N(4)−C(1*) | 117.5(6) | N(5)−C(3)−N(6) | 122.2(11) |
| N(6)−S(4)−C(23) | 100.8(3) | S(1*)−N(1*)−C(1*) | 127.4(6) | N(7)−C(4)−N(8) | 120.5(1) |
| S(1)−N(1)−C(1) | 110.8(5) | N(3)−C(15)−N(2) | 121.9(6) | N(1)−C(1)−N(2) | 119.6(11) |
| S(2)−N(3)−C(2) | 111.5(5) | N(1)−C(1)−N(4*) | 121.2(7) | N(3)−C(2)−N(4) | 121.5(10) |
| S(3)−N(5)−C(3) | 112.4(5) | N(1)−S(1)−N(2)−C(15) | −69.7(7) | S(3)−N(4)−C(2) | 126.2(8) |
| S(4)−N(7)−C(4) | 111.4(5) | N(2)−S(1)−N(1)−C(1) | 146.4(7) | S(3)−N(5)−C(3) | 120.4(9) |
| N(1)−C(1)−N(2) | 122.1(6) | N(3)−S(2)−N(4)−C(1*) | 75.9(7) | S(4)−N(6)−C(3) | 126.8(9) |
| N(2)−C(1)−C(29) | 123.0(7) | N(4)−S(2)−N(3)−C(15) | −156.2(7) | S(4)−N(7)−C(4) | 117.0(8) |
| N(3)−C(2)−C(36) | 114.3(6) | S(2)−N(3)−C(15)−N(2) | −164.8(6) | S(1)−N(8)−C(4) | 131.0(9) |
| N(5)−C(3)−N(6) | 121.2(6) | S(1*)−N(1*)−C(1*)−N(4) | 179.5(6) | S(1)−N(1)−C(1) | 118.3(8) |
| N(6)−C(3)−C(43) | 126.8(6) | S(1*)−N(2*)−C(15*)−N(3*) | 1.8(11) | S(2)−N(2)−C(1) | 131.5(9) |
| N(7)−C(4)−C(50) | 112.9(6) | | | S(2)−N(3)−C(2) | 117.5(8) |
| N(1)−S(1)−C(5) | 97.6(3) | | | | |
| N(2)−S(2)−N(3) | 107.1(3) | | | | |
| N(3)−S(2)−C(11) | 97.9(3) | | | | |
| N(4)−S(3)−C(17) | 99.1(3) | | | | |
| N(6)−S(4)−N(7) | 109.0(3) | | | | |
| N(7)−S(4)−C(23) | 97.1(3) | | | | |
| S(2)−N(2)−C(1) | 116.5(5) | | | | |
| S(3)−N(4)−C(2) | 116.6(5) | | | | |
| S(4)−N(6)−C(3) | 117.3(5) | | | | |
| S(1)−N(8)−C(4) | 117.3(5) | | | | |
| N(1)−C(1)−C(29) | 114.8(6) | | | | |
| N(3)−C(2)−N(4) | 121.1(6) | | | | |
| N(4)−C(2)−C(36) | 124.6(6) | | | | |
| N(5)−C(3)−C(43) | 112.0(6) | | | | |
| N(7)−C(4)−C(8) | 122.5(6) | | | | |
| N(8)−C(4)−C(50) | 124.6(6) | | | | |

**X-ray Structures of 2c, 4b, and 4c.** The X-ray structure of the 16-membered ring **2a** has been described previously.[6] We have determined the structure of a second example of this macrocycle, **2c**, to provide an appropriate comparison with structural parameters of the corresponding S(VI) system **4c**. An ORTEP drawing of **2c** is shown in Figure 3. The 16-membered $C_4N_8S_4$ ring adopts a cradlelike structure with approximate $S_4$ symmetry, similar to that of **2a**.[6] An ORTEP plot for **4c** is shown in Figure 4. The cradle conformation of the $C_4N_8S_4$ ring is retained upon oxidation, but the central cavity opens up. As a result, the N−N distance is 5.05 Å in the S(VI) system **4c** compared to 3.96 Å in **2c**. The S−S separations also increase from 5.54 to 6.05 Å upon oxidation. Similar structural effects are also observed for **4b** with N−N and S−S separations of 4.35 and 5.77 Å, respectively.

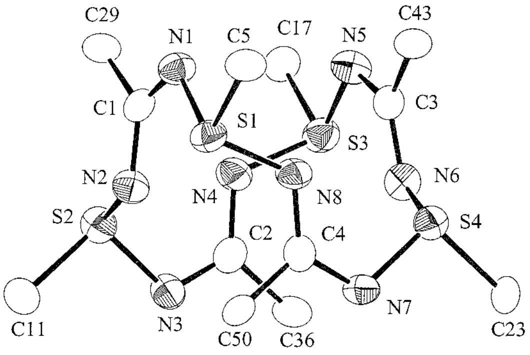

**Figure 3.** ORTEP drawing of $(4\text{-}CH_3C_6H_4)_4C_4N_8S_4Ph_4$ (**2c**). For clarity only α-carbon atoms of aryl groups attached to the C and S atoms of the heterocyclic ring are shown.

The structural parameters for **2c**, **4b**, and **4c** are given in Table 7. Comparison of the mean values of bond lengths and bond angles for **2c** and **4c** reveals trends similar to those noted for eight-membered $C_2N_4S_2$ rings. Upon oxidation, the S−N bond

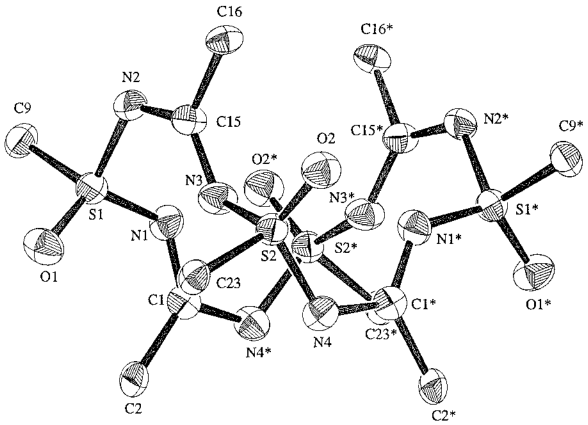

**Figure 4.** ORTEP drawing of (4-$CH_3C_6H_4)_4C_4N_8S_4O_4Ph_4$ (**4c**). For clarity only α-carbon atoms of aryl groups attached to the C and S atoms of the heterocyclic ring are shown.

lengths decrease by ca. 0.07 Å (from 1.664 to 1.595 Å) while the C−N distances remain essentially unchanged. The bond angles ∠SNC widen by ca. 8°, whereas ∠NCN is unaffected.

Finally, we note that 12- and 24-membered rings involving PNPNS(VI)N units have been isolated and structurally characterized as minor products in the ROP of the corresponding six-membered heterocycles.[25] The 16-membered rings **4b**,**c** are, however, unique among sulfanuric systems.

## Conclusion

Eight- and 16-membered cyanuric−sulfanuric ring systems are readily prepared in good yields by the oxidation of the corresponding S(IV) systems. Oxidation induces a contraction of the S−N bonds by ca. 0.06 Å but only minor distortions to the boat and cradle conformations of these heterocycles. A novel, thermally induced ring contraction involving the elimination of a sulfanuric group was observed for the eight-membered rings.

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**Supporting Information Available:** X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998.