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Six-Membered Cyanuric-Thiazyl and Cyanuric-Sulfanuric Ring Systems: Thermal Isomerization of $(CF_3CH_2O)_3C_2N_3S(O)$ to $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3S(O)_2$

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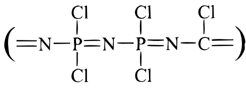
^{13}C NMR spectra of the reaction of $Cl_3C_2N_3S$ (**7**) with NaOPh in THF in various molar ratios show that nucleophilic substitution occurs preferentially at sulfur and, for a 1:3 molar ratio, produces $(PhO)_3C_2N_3S$ cleanly. The monosubstituted derivative $Cl_2C_2N_3S(OC_6H_4Ph\text{-}2)$ was prepared from **7** and $NaOC_6H_4C_6H_5\text{-}2$ in a 1:1 molar ratio in dioxane. The reaction of **7** with 3 equiv of NaOR (R = CH_3, C_2H_5, CH_2CF_3) in diethyl ether produces the trisubstituted derivatives $(RO)_3C_2N_3S$ as colorless liquids, which were characterized by IR, ^{13}C NMR, and mass spectra. The thermolysis of **7** at 220 °C for 4 h gives a viscous, transparent orange gum with the loss of sulfur chlorides. The oxidation of **7** with a mixture of $KMnO_4$ and $CuSO_4\cdot xH_2O$ ($x = 4-6$) in CH_2Cl_2 yields the new hybrid cyanuric−sulfanuric system $Cl_3C_2N_3S(O)$ (**8**) as a low melting solid, which was characterized by IR, ^{13}C NMR, and mass spectra. The thermolysis of $(CF_3CH_2O)_3C_2N_3S(O)$, prepared by the reaction of **8** with 3 equiv of $NaOCH_2CF_3$ in CH_2Cl_2, at 175 °C for 5 days results in an O → N migration of a CH_2CF_3 group to give $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3S(O)_2$ (**14**). The X-ray structure of **14** shows that this CH_2CF_3 group is attached to the unique nitrogen atom of a planar C_2N_3S ring. Crystals of **14** are triclinic, space group P with $a = 11.931(2)$ Å, $b = 10.949(2)$ Å, $c = 22.063(6)$ Å, $\alpha = 89.97(2)°$, $\beta = 90.36(2)°$, $\gamma = 90.04(1)°$, $V = 2882.1(9)$ Å^3, and $Z = 8$.

Introduction

Inorganic polymers involving p-block elements in the backbone have been investigated extensively in recent years. One of the classic examples, $(NPCl_2)_n$, has P−N repeating units in the polymer chain. Such polymers, known as poly(phosphazenes), have a wide range of applications based on their unique properties, e.g. water-repellency, flexibility, and nonflammability. Recently, inorganic polymers consisting of PNPNCN[2] or PNPNSN[3] repeating units, e.g. **1** and **2**, have been characterized. Ring-opening polymerization (ROP) is the method of choice for the production of these hybrid backbone systems.[4−11]

The chlorinated cyanuric (**3**), thiazyl (**4**), and sulfanuric (**5**) ring systems have been known for many years, but ROP does not produce polymers from these well-known heterocycles. The sulfur(IV) system **4** dissociates into NSCl monomer both in the gas phase[12] and in solution,[13] while the sulfur(VI) system (**5**) decomposes exothermically above 250 °C.[14] However, sulfanuric polymers $[NS(O)R]_n$ (R = Me, Et, Ph) have been prepared by a condensation route.[15]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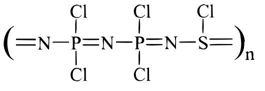
$$\left(=N-\underset{Cl}{\overset{Cl}{P}}=N-\underset{Cl}{\overset{Cl}{P}}=N-\overset{Cl}{S}=\right)_n$$

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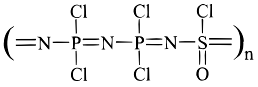
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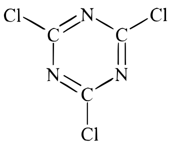

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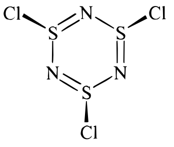

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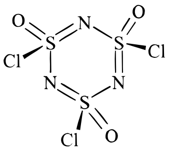

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The hybrid cyanuric−thiazyl rings, **6** and **7**, and the cyanuric-sulfanuric system **8** are potential sources of CN/SN polymers via ROP. However, the thermolysis of **6** [R = ^tBu, Ph, CCl_3, NR'_2 (R′ = Me, Et, ^iPr)] at 40−110 °C results in ring contraction

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(1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(2) (a) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478. (b) Allcock, H. R.; Coley, S. M.; Manners, I.; Nuyken, O.; Renner, G. *Macromolecules* **1991**, *24*, 2024.

(3) Ni, Y.; Park, P.; Liang, M.; Massy, J.; Waddling, C.; Manners, I. *Macromolecules* **1996**, *29*, 3401.

(4) Dodge, J. A.; Manners, I.; Renner, G.; Allcock, H. R.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268.

(5) Allcock, H. R.; Dodge, J. A.; Manners, I.; Renner, G.; Nuyken, O. *Macromolecules* **1993**, *26*, 11.

(6) Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109.

(7) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044.

(8) Liang, M.; Manners, I. *Makromol. Chem., Rapid Commun.* **1991**, 613.

(9) Ni, Y.; Stammer, A.; Liang, M.; Massey, J.; Vancso, G. J.; Manners, I. *Macromolecules* **1992**, *25*, 7119.

(10) Jaeger, R.; Lagowski, J. B.; Manners, I.; Vancso, G. J. *Macromolecules* **1995**, *28*, 9.

(11) Ni, Y.; Lough, A. J.; Rheingold, A. L.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 998.

(12) Patton, R. L.; Jolly, W. L. *Inorg. Chem.* **1970**, *9*, 1079.

(13) Passmore, J.; Schriver, M. J. *Inorg. Chem.* **1988**, *27*, 2751.

(14) McKenney, R. L.; Fetter, N. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3569.

(15) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigorias, S. *J. Am. Chem. Soc.* **1993**, *115*, 2604. These authors suggest the name poly(oxothiazenes) for polymers of the type $[NS(O)R]_n$.

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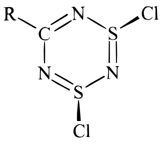
to give the corresponding five-membered rings $RCN_2S_2^+Cl^-$.[16] The heterocycle **7** was first described in 1970, but at that time an acyclic structure was inferred.[17] The cyclic structure was not established until 1976,[18] and the X-ray structure was described in 1993.[19a] The structure of the corresponding trifluoro derivative $F_3C_2N_3S$ has also been determined by electron diffraction.[19b] There are no reports of attempts to polymerize **7** and the corresponding sulfur(VI) heterocycle **8** is unknown.



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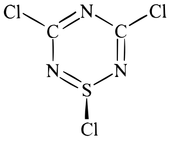

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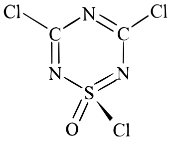

8

In this article we report (a) investigations of the regiospecificity of the reaction of **7** with nucleophiles, (b) the preparation and spectroscopic characterization of $Cl_2C_2N_3S(OC_6H_4C_6H_5\text{-}2)$ and $C_2N_3S(OR)_3$ (R = Me, Et, CH_2CF_3), (c) the synthesis and spectroscopic characterization of **8**, (d) attempted ROP of **7** and **8**, and (e) a novel thermal isomerization of $(CF_3CH_2O)_3\text{-}C_2N_3S(O)$.

Experimental Section

The reagents sodium dicyanamide, tetramethylammonium chloride, CF_3CH_2OH, *o*-phenylphenol, $CuSO_4{\cdot}xH_2O$ ($x = 4-6$, Aldrich), *m*-chloroperbenzoic acid (MCPBA), $KMnO_4$, and $^nBu_4N[MnO_4]$ were obtained from commercial sources. CF_3CH_2OH was distilled over Drierite and $NaHCO_3$ and stored over molecular sieves. $NaOCH_2CF_3$ was prepared by the reaction of CF_3CH_2OH with Na metal in THF. Thionyl chloride was distilled before use. CH_3OH was distilled over Drierite and stored over molecular sieves. Other solvents were dried with the appropriate drying agents and distilled immediately before use. The reactions and manipulation of moisture-sensitive compounds were carried out under an atmosphere of dinitrogen.

^1H and ^{13}C NMR spectra were recorded on a Bruker ACE spectrometer and chemical shifts are reported relative to Me_4Si in $CDCl_3$. Infrared spectra were obtained as Nujol mulls on a Mattson 4030 FTIR spectrophotometer. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary. Mass spectra (EI, 70 eV) were measured on a Kratos MS80RFA instrument. GC/MS were obtained by using a Hewlett-Packard 5890 spectrometer.

Preparation of $Cl_3C_2N_3S$ (7). The heterocycle **7** was prepared by the reaction of $NaN(CN)_2$ with $SOCl_2$ in DMF in the presence of Me_4NCl according to the literature[17] except that 40 mL of dry diethyl ether was used to extract the product from the reaction mixture. The solvent was removed under vacuum and pure **7** was obtained in ca. 60% yield by sublimation at 23 °C/10^{-2} Torr. ^{13}C NMR: δ (in $CDCl_3$) 170.2; (in THF-d_8) 170.6. MS (*m*/*z*, %): 168 (50, $M - Cl^+$), 107 (30, $M - Cl_2CN^+$), 87 (35), 72 (15), 61 (17, $ClCN^+$), 46 (100, NS^+). IR (cm^{-1}, NaCl plates): 1527 s, 1484 vs, 1438 vs, 1370 vs, 1340 vs, 1234 s, 1196 s, 1109 m, 994 m, 861 s, 831 s, 816 s, 759 s, 736 vs.

Reaction of $Cl_3C_2N_3S$ (7) with NaOPh. A solution of NaOPh in THF was added dropwise (2−3 h) to a stirred solution of **7** in THF at 23 °C. The reaction mixture was centrifuged, and the precipitate of NaCl was removed by filtration. Solvent was removed under vacuum, and the ^{13}C NMR spectrum of a solution of the residue in $CDCl_3$ was recorded. This procedure was repeated for four different molar ratios (see Figure 1).

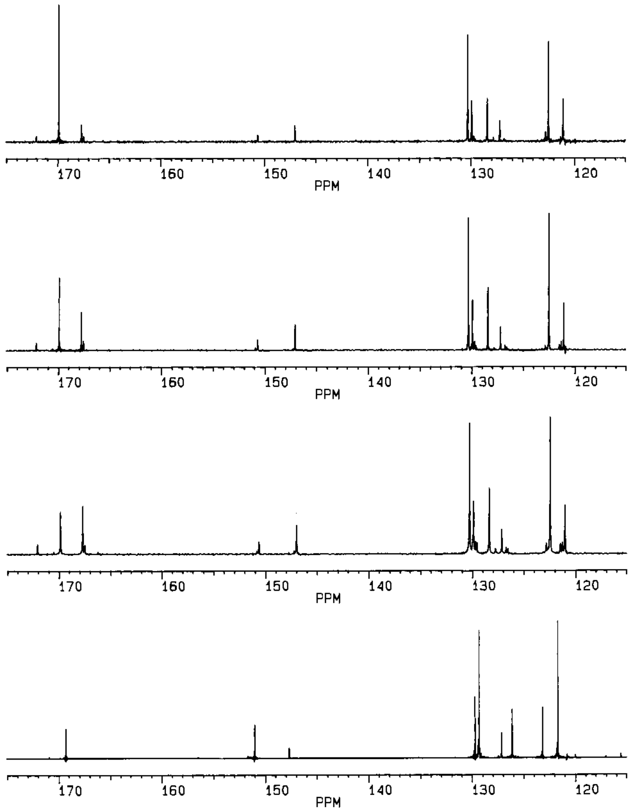

Figure 1. ^{13}C NMR spectra (in $CDCl_3$) for the products of the reaction $Cl_3C_2N_3S$ (**7**) with NaOPh in THF in different molar ratios: (a) 1:0.3, (b) 1:0.7, (c) 1:1, (d) 1:3.

Thermal ROP of $Cl_3C_2N_3S$ (7). Attempted thermal ROP experiments were performed at several temperatures between 180 and 220 °C. The results were similar, but the reaction times (as judged by the formation of an immobile product) were, as expected, slower at the lower temperature (24 h at 180 °C, 4 h at 220 °C). The following procedure is representative.

Solid $Cl_3C_2N_3S$ (2.53 g, 12.4 mmol) was heated in a sealed evacuated Pyrex tube at 220 °C. After 4 h the molten material had become immobile. The tube was opened in the glovebox and the contents were extracted with dioxane (150 mL). A small amount of apparently insoluble, but swollen, cross-linked polymeric material remained. To the dioxane solution cooled to 0 °C was added a solution of $Na[OC_6H_4Ph\text{-}p]$ (13.2 g, 68.7 mmol) in dioxane (200 mL). After stirring at 25 °C for an additional 2 h, Me_3SiCl (3.4 mL, 27 mmol) was added to quench unreacted aryloxide and the reaction mixture was stirred for 15 min. The solvent was then removed to yield an orange gel-like mass. The resulting product was purified by precipitation from dioxane into water (twice) and then from CH_2Cl_2 into (hexanes) to yield white strands which formed a white powder when dried. Yield 2.2 g (29% based on the idealized formula $[C_2N_3S(OC_6H_4Ph\text{-}p)_3]_n$). The ^{13}C NMR spectrum of the product (in CD_2Cl_2) showed a complex series of broad resonances in the 120−170 ppm region.

GPC. No eluted peaks were detected using a refractive index detector with cross-linked polystyrene columns in THF. We attribute this to absorption of the product on the GPC column. A preliminary investigation by dynamic light scattering suggested the presence of large structures with an approximate size consistent with a molecular weight of ca. 10^6.

Preparation of $Cl_3C_2N_3S(O)$ (8). A finely ground mixture of $KMnO_4$ (8 g) and $CuSO_4{\cdot}xH_2O$ (4 g) was added to a solution of $Cl_3C_2N_3S$ (6.28 g, 30.8 mmol) in CH_2Cl_2 (150 mL). The suspension was heated at reflux for 16 h. The reaction mixture was filtered, and water (10 mL) was added to the filtrate, which was then stirred for 5

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(16) (a) Apblett A.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1989**, 96. (b) Apblett A.; Chivers, T. *Inorg. Chem.* **1989**, *28*, 4544.

(17) Geevers, J.; Hackmann, J. Th.; Trompen, W. P. *J. Chem. Soc. (C)* **1970**, 875.

(18) Voss, G.; Fischer, E.; Rembarz, G.; Schramm, W. *Z. Chem.* **1976**, *16*, 358.

(19) (a) Chen, S.-J.; Behrens, U.; Fischer, E.; Mews, R.; Pauer, F.; Sheldrick, G. M.; Stalke, D.; Stohrer, W.-D. *Chem. Ber.* **1993**, *126*, 2601. (b) Fischer, E.; Jandas-Prezel, E.; Maggiulli, R.; Mews, R.; Oberhammer, H.; Paape, R.; Stohrer, W. D. *Chem. Ber.* **1991**, *124*, 1347.

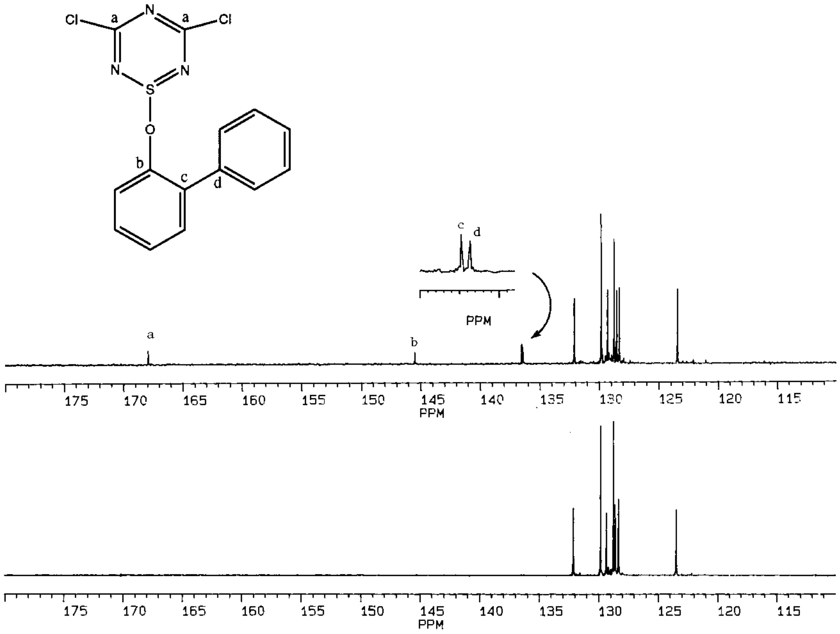

Figure 2. (a) ^{13}C NMR spectra of $Cl_2C_2N_3S(OC_6H_4Ph\text{-}2)$ **10b** in $CDCl_3$ (b) using the DEPT pulse sequence.

min. The CH_2Cl_2 layer was separated and dried ($MgSO_4$). The CH_2Cl_2 solution was cooled to −15 °C (NH_4Cl−ice bath), and the solvent was removed slowly under vacuum. Sublimation of the residue at 23 °C/10^{-2} Torr onto a cold finger cooled with dry ice gave pure $Cl_3C_2N_3S(O)$. (1.26 g, 5.71 mmol, 19%) as a white solid. Mp 20−22 °C. Anal. Calcd for $C_2N_3Cl_3OS$: C, 10.90; H, 0.00; N, 19.06. Found: C, 11.12; H. 0.01; N, 18.71. ^{13}C NMR: δ (in $CDCl_3$) 172.0; (in THF-d_8): 172.6. MS (*m*/*e*, %): 219 (5, M^+), 184 (100, M − Cl^+), 123 ($C_2N_2OSCl^+$, 7), 114 (10), 83 ($SOCl^+$, 50), 63 (5), 48 (80, SO^+). IR (cm^{-1}, NaCl plates): 1488 vs, 1377 vs, 1352 vs, 1284 s, 1213 s, 1198 s, 992 m, 868 s, 818 s, 795 s, 721 s.

Preparation of $(MeO)_3C_2N_3S$ (9b). A solution of $Cl_3C_2N_3S$ (5.50 g, 27.0 mmol) in diethyl ether (50 mL) was added slowly, with stirring to a suspension of $NaOCH_3$ (5.0 g, 90 mmol) in diethyl ether (50 mL) at 0 °C. The temperature was allowed to reach 23 °C during 2 h, and water (20 mL) was added to the suspension. The ether layer was separated and dried ($MgSO_4$), and the solvent was removed under vacuum. The product $(MeO)_3C_2N_3S$ was obtained as a colorless liquid (1.50 g, 7.9 mmol, 29%) after sublimation of the residue at 60 °C/10^{-2} Torr onto a cold finger (−78 °C). Anal. Calcd for $C_5H_9N_3O_3S$: C, 31.41; H, 4.74; N, 21.98. Found: C, 30.71; H, 3.12; N, 21.17. ^{13}C NMR (in $CDCl_3$: δ) 169.2 (*C*N_2), 54.2 (C−O*C*H_3), 48.7 (S−O*C*H_3). MS (*m*/*e*, %): 160 (100, M^+ − OCH_3). IR (liquid film, NaCl plates); 3003 w, 2965 m, 2880 w, 1548 vs, 1474 vs, 1419 vs, 1396 vs, 1367 vs, 1324 vs, 1201 s, 1129 vs, 1080 s, 1057 w, 1008 s, 959 s, 939 s, 859 s, 841 s, 784 s, 669 vs, 655 vs.

Preparation of $(EtO)_3C_2N_3S$ (9c). The derivative $(EtO)_3C_2N_3S$ was obtained as a colorless liquid (4.46 g, 19.1 mmol, 71%) from the reaction of $Cl_3C_2N_3S$ (5.5 g, 27.0 mmol) and $NaOCH_2CH_3$ (8.2 g, 120 mmol) by a procedure similar to that described for **9b**. Anal. Calcd for $C_8H_{15}N_3O_3S$: C, 41.19; H, 6.49; N, 18.02. Found: C, 41.46; H, 6.74; N, 18.40. ^{13}C NMR (in $CDCl_3$, δ): 168.4 (*C*N_2), 63.0 (C−O*C*H_2CH_3), 59.5 (S−OCH_2CH_3), 14.9 (S−O*C*H_2CH_3), 13.9 (C−OCH_2*C*H_3). MS (*m*/*e*, %): 188 (75, M^+ − OCH_2CH_3). IR (liquid film, NaCl plates); 2993 m, 2935 w, 1541 vs, 1473 s, 1425 vs, 1383 s, 1338 s, 1313 vs, 1168 m, 1123 vs, 1075 m, 1059 w, 1004 vs, 927 w, 914 w, 879 s, 824 s, 783 s.

Preparation of $(CF_3CH_2O)_3C_2N_3S$ (9d). Solid $NaOCH_2CF_3$ (5.4 g, 44.3 mmol) was added slowly to a stirred solution of $Cl_3C_2N_3S$ (3.0 g, 14.7 mmol) in CH_2Cl_2 (40 mL) at 0 °C. After 2 h the reaction mixture was filtered. Water (20 mL) was added to the filtrate. The CH_2Cl_2 layer was separated and dried over $MgSO_4$. Removal of solvent at 23 °C gave $(CF_3CH_2O)_3C_2N_3S$ as a colorless liquid (4.6 g, 11.6 mmol, 79%). Anal. Calcd for $C_8H_6N_3F_9O_3S$: C, 24.31, H, 1.53; N, 10.63. Found: C, 24.51; H, 1.37; N. 10.76. ^{13}C NMR (in $CDCl_3$): δ 168.5 (*C*N_2), 122.8 (C−OCH_2*C*F_3, q, $^1J_{CF}$ = 277.2 Hz), 122.6 (S−OCH_2*C*F_3, q, $^1J_{CF}$ = 277.9 Hz), 63.5 (C−O*C*H_2CF_3, q, $^3J_{CF}$ = 37.2 Hz), 61.9 (S−O*C*H_2CF_3, q, $^3J_{CF}$ = 37.7 Hz). MS (*m*/*e*, %): 376 (5, M^+ − F), 296 (100, M^+ − OCH_2CF_3). IR (liquid film, NaCl plates): 2978 w, 1563 vs, 1465 vs, 1436 vs, 1393 s, 1352 s, 1269 vs, 1178 vs, 1141 vs, 1106 s, 1022 s, 999 s, 965 vs, 868 s, 857 s, 839 s, 781 vs.

Preparation of $Cl_2C_2N_3S(OC_6H_4Ph\text{-}2)$ (10b). A solution of $NaOC_6H_4C_6H_5$-2, prepared from *o*-phenylphenol (1.50 g, 8.8 mmol) and Na metal (0.30 g) in dioxane, was added dropwise into a stirred solution of $Cl_3C_2N_3S$ (1.80 g, 8.8 mmol) in dioxane (10 mL) over a period of 6 h. Solvent was removed under vacuum, and the orange oily product was extracted several times with hexane. Removal of hexane under vacuum gave $Cl_2C_2N_3S(OC_6H_4Ph\text{-}2)$ (0.86 g, 2.3 mmol, 26%) as a white solid. Anal. Calcd for $C_{14}H_9N_3Cl_2OS$: C, 49.72; H, 2.68; N, 12.42. Found: C, 49.28; H, 2.74; N, 12.47. ^{13}C NMR (in $CDCl_3$): δ 167.9 (*C*N_2), 145.4 [SO*C* (phenoxyl)], 136.3 [phenoxyl*C*-C(phenyl)], 136.5 [phenoxylC-*C*(phenyl)] (see Figure 2).

Preparation of $(CF_3CH_2O)_3C_2N_3S(O)$ (13). Solid $NaOCH_2CF_3$ (2.50 g, 20.5 mmol) was added slowly to a stirred solution of $Cl_3C_2N_3S(O)$ (1.20 g, 5.44 mmol) in CH_2Cl_2 (20 mL) at −15 °C. The suspension was stirred for 2 h and then filtered. Solvent was removed from the filtrate under vacuum, and the residue was sublimed at 70 °C/10^{-2} Torr to give $(CF_3CH_2O)_3C_2N_3S(O)$ (1.90 g, 4.62 mmol, 85%). The product was collected on a cold finger cooled by dry ice. It is a colorless liquid at 23 °C. Anal. Calcd for $C_8H_6N_3F_9O_4S$: C, 23.37; H, 1.47; N, 10.22. Found: C. 23.59; H. 1.38; N, 10.43. ^{13}C NMR (in $CDCl_3$): δ 169.9 (*C*N_2), 122.5 (C−OCH_2*C*F_3, q, $^1J_{CF}$ = 277.2 Hz), 121.7 (S−OCH_2*C*F_3, q, $^1J_{CF}$ = 277.6 Hz), 66.7 (S−O*C*H_2CF_3, $^3J_{CF}$ = 39.0 Hz), 64.4 (C−O*C*H_2CF_3, q, $^3J_{CF}$ = 37.7 Hz). MS (*m*/*e*, %): 411 (25, M^+), 392 (15, M^+ − F), 342 (3, M^+ − CF_3), 312 (30, M^+ − OCH_2CF_3), 213 (100, M^+ − $2OCH_2CF_3$), 147 (70, $SO_2CH_2CF_3^+$), 83 (80, CH_2CF_3), 69 (15, CF_3). IR (cm^{-1}, NaCl plates): 3052 w, 2992 w, 1563 vs, 1473 vs, 1439 vs, 1403 m, 1372 m, 1329 s, 1270 vs, 1177 vs, 1149 vs, 1116 m, 1028 s, 997 s, 964 s, 921 m, 882 m, 857 m, 775 m.

Preparation of $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3SO_2$ (14). A sample of $(CF_3CH_2O)_3C_2N_3S(O)$ (1.80 g, 4.38 mmol) was heated at 175 °C for 5 days in a thick-walled glass tube that had been sealed under vacuum. Upon cooling to room temperature the liquid contents of the tube formed colorless crystals. A pure sample of $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3SO_2$ (1.50 g, 3.65 mmol, 83%) was obtained by slow evaporation of a CH_2Cl_2 solution. Mp 153−156 °C. Anal. Calcd for $C_8H_6N_3F_9O_4S$: C, 23.37; H, 1.47; N, 10.22. Found: C, 23.48; H, 1.35; N, 10.20. ^{13}C NMR (in $CDCl_3$): δ 150.7 (*C*N_2), 122.7 (NCH_2*C*F_3, q, $^1J_{CF}$ = 279.9 Hz), 122.4 (C−OCH_2*C*F_3, q, $^1J_{CF}$ = 277.2), 66.5 (C−O*C*H_2CF_3, q, $^3J_{CF}$ = 38.2 Hz), 45.3 (N-*C*H_2CF_3), $^3J_{CF}$ = 37.7 Hz). MS (*m*/*e*, %): 411

Table 1. Crystallographic Data for $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3SO_2$ (**14**)

empirical formula	$C_8H_6F_9O_4N_3S$
fw	411.20
space group	$P\bar{1}$ (No. 2)
a, Å	11.931 (2)
b, Å	10.949 (2)
c, Å	22.063 (6)
α, deg	89.97 (2)
β, deg	90.36 (2)
γ, deg	90.04 (1)
V, Å^3	2882.1 (9)
Z	8
T, °C	−103
λ, Å	0.710 69
ρ_{calcd}, g cm^{-3}	1.89
μ, cm^{-1}	3.55
R^a	0.063
$R_w{}^b$	0.083

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

(45, M$^+$), 392 (20, M$^+$ − F), 265 (40), 207 (47), 126 (100), 83 (90), 69 (25, $CF_3{}^+$). IR: 1718 vs, 1702 vs, 1580 vs, 1434 vs, 1403 vs, 1348 vs, 1286 vs, 1241 s, 1214 vs, 1195 vs, 1173 vs, 1131 s, 1033 vs, 995 m, 961 s, 942 m, 856 s, 839 s, 775 s, 732 s, 710 s.

X-ray Analysis. A suitable colorless, prismatic crystal of **14** with dimensions 0.40 × 0.30 × 0.22 mm was mounted on a glass fiber. Accurate cell dimensions and a crystal orientation matrix were obtained on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 25 reflections with 2θ in the range 20−30°. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 8.0° min^{-1}, scan width $(0.73 + 0.34 \tan \theta)°$, and monochromated Mo Kα radiation in the range $4.0° < 2\theta < 50.1°$.

The intensities of 9566 reflections were measured, of which 8818 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects. Crystal data are given in Table 1. The angles α and γ are ca. 90°, therefore the crystal system was checked for a monoclinic lattice. A 2-fold axis parallel to the b axis was found to be absent as the agreement between hkl and $\bar{h}k\bar{l}$ reflections was >0.718. A mirror plane perpendicular to the a axis was also absent as the agreement between hkl and $\bar{h}kl$ reflections was >0.664. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods[20] and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Scattering factors were those of Cromer and Waber,[22] and allowance was made for anomalous dispersion.[23] All calculations were performed using teXsan.[24]

Results and Discussion

Model Reactions of Trichlorothiatriazine (7) with Sodium Alkoxides and Aryloxides. Chlorinated inorganic polymers of the type **1** and **2**, especially the S(IV) derivative **2a**, are moisture-sensitive.[6] Hydrolytically stable materials may, however, be obtained by reaction with aryloxide nucleophiles.[4] Interestingly, the regiospecificity of these substitutions is different for the hybrid S(IV) and S(VI) polymers.[4,7] In the former case substitution occurs preferentially at sulfur whereas the reverse is true for the S(VI) systems, for which aryloxide substitution occurs only at phosphorus and the S−Cl bonds remain intact. By contrast, no regiospecificity was observed for the CN/PN system **1** or its cyclic precursor in reactions with aryloxides,[2] but Shreeve et al. have recently reported regiospecificity with N-centered nucleophiles.[25]

^{31}P NMR provides an excellent probe for the formation of the polymers **1**, **2a**, and **2b** by ROP. The transformation of rings to polymers is accompanied by a shift of ca. 40 ppm to higher field. For the hybrid CN/SN ring systems **7** and **8**, ^{13}C NMR is the only reasonable choice for monitoring ROP. In light of this background our investigations of the polymerization of **7** began with model studies of the reaction of this heterocycle with sodium aryloxides and alkoxides in order to (a) establish the regiospecificity of nucleophilic substitution and (b) provide information to assist in the ^{13}C NMR assignments of polymers.

The reaction of **7** with sodium phenoxide in THF was carried out for molar ratios ranging from 1:0.3 to 1:3. The ^{13}C NMR spectra of the reaction mixtures are compared in Figure 1. The ^{13}C NMR spectrum of the 1:3 product (Figure 1d) is consistent with the formation of the pure, trisubstituted product $(PhO)_3C_2N_3S$ (**9a**). The ^{13}C chemical shift of the ring carbon atoms changes from 170.2 ppm in **7** to 169.2 ppm in **9a**. The C_6H_5O group will exhibit four resonances in the ^{13}C NMR spectrum and these should appear with relative intensities of 2:1 for the carbon-attached and sulfur-attached PhO groups, respectively. Consistently, the set of six resonances in the 120−130 ppm region shows the expected pattern. On the basis of relative intensities, the high-field signals in each of the three pairs of resonances are assigned to the carbon-attached OPh groups. The middle pair of resonances at δ 126−127 ppm is ascribed to the *para*-C atoms. The two resonances at ca. δ 148 and 151 ppm are attributed to the phenyl carbons linked to oxygen. For this pair of resonances, the relative intensities suggest that the high-field signal belongs to the OPh group attached to sulfur.

Inspection of the ^{13}C NMR spectra for the 1:0.3, 1:0.7, and 1:1 molar ratios (Figure 1a−c) reveals some informative trends. The relative intensities of the pairs of resonances observed in the δ 120−130 and δ 150 ppm regions are reversed compared to those found for the 1:3 molar ratio (Figure 1d) implying preferential, but not exclusive, substitution at sulfur. Consistently, there are three resonances in the δ 168−172 ppm region, in addition to the strong signal for unreacted **7** at δ 170.2 ppm, none of which corresponds to the ring carbon atoms of **9a** (δ 169.2 ppm). For the 1:1 molar ratio (Figure 1c), the intense resonance at δ 168.0 ppm can be attributed to the monosubstituted product **10a**, while the pair of equally intense signals at δ 172.2 and 167.8 ppm is assigned to the unsymmetrical disubstituted derivative **11**.

To confirm the preferential substitution at sulfur, the reaction of **7** with $NaOC_6H_4Ph$-2 was carried out in a 1:1 molar ratio in dioxane. An analytically pure sample of composition $(2\text{-}OC_6H_4Ph)Cl_2C_2N_3S$ was obtained and the ^{13}C NMR spectrum of this product confirmed it to be **10b**, i.e., exclusive substitution at sulfur (see Figure 2a). Single resonances are observed at δ 167.9 ppm for the heterocyclic ring carbons and at δ 145.4 ppm for the O-bonded carbon atom. The assignments of the quaternary carbons in **10b** were confirmed by using the DEPT pulse sequence (Figure 2b).

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(20) SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1993**, *26*, 343.

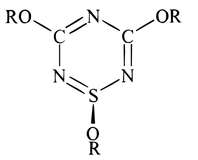
(21) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands. 1994.

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

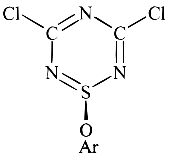
(23) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(24) *teXsan, Single-Crystal Structure Analysis Software*, Version 1.2; Molecular Structure Corp.: The Woodlands, TX, 1992.

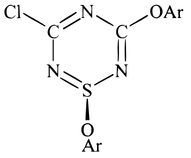
(25) Vij, A.; Elias, A. J.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1997**, *36*, 2730.



9a (R = OPh)
9b (R = OMe)
9c (R = OEt)
9d (R = OCH_2CF_3)



10a (Ar = OPh)
10b (Ar = 2-OC_6H_4Ph)

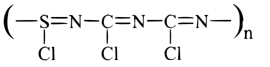


11

The series of trialkoxy-substituted derivatives **9b**−**d** was obtained as air-stable, colorless liquids in yields of 29% (**9b**), 52% (**9c**), and 80% (**9d**) by the reaction of **7** with the appropriate sodium alkoxide in a 1:3 molar ratio in diethyl ether at 0 °C. The products were characterized by CHN analyses, IR and mass spectra, and their characteristic ^{13}C NMR spectra which exhibited singlets at δ 168−169 ppm for ring carbons as well as separate resonances for the alkoxy groups attached to carbon and sulfur. The parent ion in the mass spectra of **9b**−**d** results from loss of one alkoxy group (presumably that attached to sulfur) from the molecular ion.

In summary, these model studies show that the reaction of **7** with sodium aryloxides occurs regiospecifically at sulfur. In addition, complete substitution of the Cl substituents in **7** by aryloxy or alkoxy groups can be achieved without degradation of the heterocyclic ring.

Attempted ROP of $Cl_3C_2N_3S$ (7). Thermal ROP of **7** in the temperature range 180−220 °C was investigated in attempts to generate the hybrid polymer **12**. In all experiments the pale yellow liquid deepened in color and became extremely viscous over this period of time. The final product was an orange, moisture-sensitive transparent gum and the formation of volatile sulfur chlorides was indicated by pressure build-up in the evacuated reaction tubes (and by their characteristic smell). The gummy product was treated with a variety of sodium aryloxides, NaOAr (Ar = Ph, C_6H_4Ph-*p*, C_6H_4Ph-*o*), $NaOCH_2CF_3$, and $C_6H_5NH_2$ in attempts to obtain a tractable polymer. However, a pure product could not be isolated (^{13}C NMR spectra) and elemental analysis revealed lower sulfur content than expected, consistent with the loss of sulfur during ROP.[26] In view of the highly moisture-sensitive nature of the product obtained from ROP of **7** (and the aryloxide derivatives), we turned our attention to the synthesis of the cyanuric−sulfanuric ring **8**. Previous studies with hybrid PN/SN systems have shown that the S(VI)-containing polymers exhibit greater hydrolytic stability than their S(IV) counterparts.[2,7]



$$\left(-\underset{\text{Cl}}{\underset{|}{S}}=N-\underset{\text{Cl}}{\underset{|}{C}}=N-\underset{\text{Cl}}{\underset{|}{C}}=N-\right)_n$$

12

Preparation and Spectroscopic Characterization of $Cl_3C_2N_3S(O)$ (8). The oxidation of the S(IV) ring system **7** to its S(VI) analogue **8** presents a challenge because of the reactive S−Cl bond in **7**. We have found MCPBA to be an effective reagent for the S(IV)−S(VI) transformation for unsaturated eight-membered ($P_2N_4S_2$[27] and $C_2N_4S_2$[28]) and sixteen-membered ($C_4N_8S_4$) rings.[28] However, the attempted oxidation of **7** by MCPBA was unsuccessful and negative results were also obtained for $KMnO_4$ in acetone or THF. The use of ^{n}Bu$_4$N[MnO$_4$] in CH_2Cl_2 provided the first indication of an oxidized product. The ^{13}C NMR spectrum revealed a small resonance at δ 172.0 ppm in addition to the predominant signal at δ 170.2 ppm for unreacted **7**. Surprisingly, the most successful reagent for the conversion **7** → **8** found to date is a mixture of $KMnO_4$ and $CuSO_4 \cdot xH_2O$ (x = 4−6) in CH_2Cl_2.[29] The use of a hydrated salt is intuitively undesirable in view of the hydrolytic sensitivity of **7** and the optimum yield of **8** is ≤20% (ca. 1 g of **8** is obtained from 5 g of **7**). However, no oxidation occurred when anhydrous $CuSO_4$ was used instead of the hydrated salt.

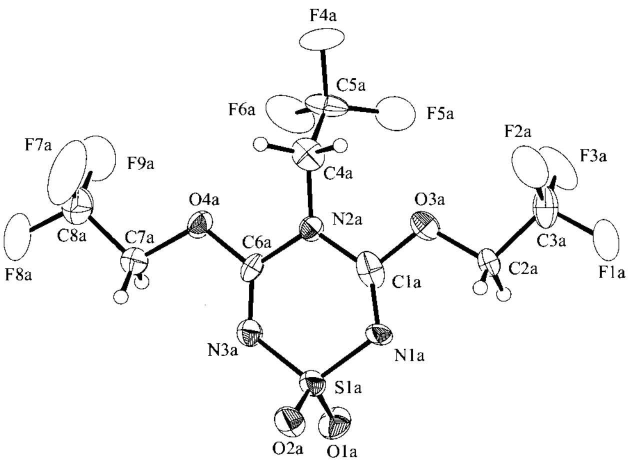


Figure 3. ORTEP drawing of $(CF_3CH_2)_2(CF_3CH_2)C_2N_3SO_2$. Only one (**14a**) of the four independent molecules in the asymmetric unit is shown.

The new cyanuric−sulfanuric ring system is obtained as a white solid by sublimation on to a cold finger at −78 °C. In view of the volatile nature of both **7** and **8**, the purity of **8** can be checked by GCMS. A pure sample of **8** melts at 20−22 °C, i.e., it is a liquid at ambient temperature. It exhibits a singlet in the ^{13}C NMR spectrum at δ 172.0 ppm (in $CDCl_3$) or δ 172.6 ppm (in THF-d_8), i.e., ca. 2.0 ppm downfield from the ^{13}C NMR resonance for **7**. Thus ^{13}C NMR also provides a quick confirmation of the purity of **8**. The EI mass spectrum of **8** exhibits a molecular ion in *m*/*z* 219 with the appropriate isotope pattern for three chlorine atoms. The parent ion is observed at *m*/*z* 188 (M − Cl$^+$). Comparison of the IR spectra of **7** and **8** leads to the assignment of a strong bond at 1284 cm^{-1} for **8** to υ(SO).

The thermal ROP of **8** in the temperature range 160−200 °C was investigated. As in the case of **7** pure products could not be isolated apparently because of the partial loss of sulfur during the ring-opening process.

Preparation and Thermal Isomerization of $(CF_3CH_2O)_3C_2N_3S(O)$ (13). Trialkoxy derivatives of the S(VI) ring could not be obtained by the oxidation of **9b**−**d** with $KMnO_4/CuSO_4 \cdot xH_2O$. However, the reaction of **8** with $NaOCH_2CF_3$ (1:3 molar ratio) in CH_2Cl_2 produced $(CF_3CH_2O)_3C_2N_3S(O)$ (**13**) as a colorless liquid in excellent yields. The heterocycle **13** exhibits a molecular ion in the EI mass spectrum and the parent ion occurs at *m*/*z* 213 (M$^+$ − $2OCH_2CF_3$). The ^{13}C NMR spectrum of **12** shows a singlet at δ 169.9 ppm for the ring carbon atoms and two sets of 1:3:3:1 quartets at ca. δ 122 ppm (*C*F$_3$) and δ 64−67 ppm (*C*H$_2$) for the CH_2CF_3 groups. The OCH_2CF_3 groups attached to carbon are readily distinguished from that attached to sulfur on the basis of relative intensities (see Experimental Section).

The thermolysis of a sample of **13** in a sealed, evacuated glass tube at 175 °C for 5 days produced colorless crystals (mp

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(26) Anal. Calcd for $C_2Cl_3N_3S$: S, 15.68. Found: S, 13.17.
(27) Brock, M.; Chivers, T.; Parvez, M. *Inorg. Chem.* **1998**, *37*, 3263.
(28) Chivers, T.; Hirsch, M.; Parvez, M. Unpublished results.
(29) Nowreldin, N. A.; McConnell, W. B.; Lee, D. G. *Can. J. Chem.* **1984**, *62*, 2113.

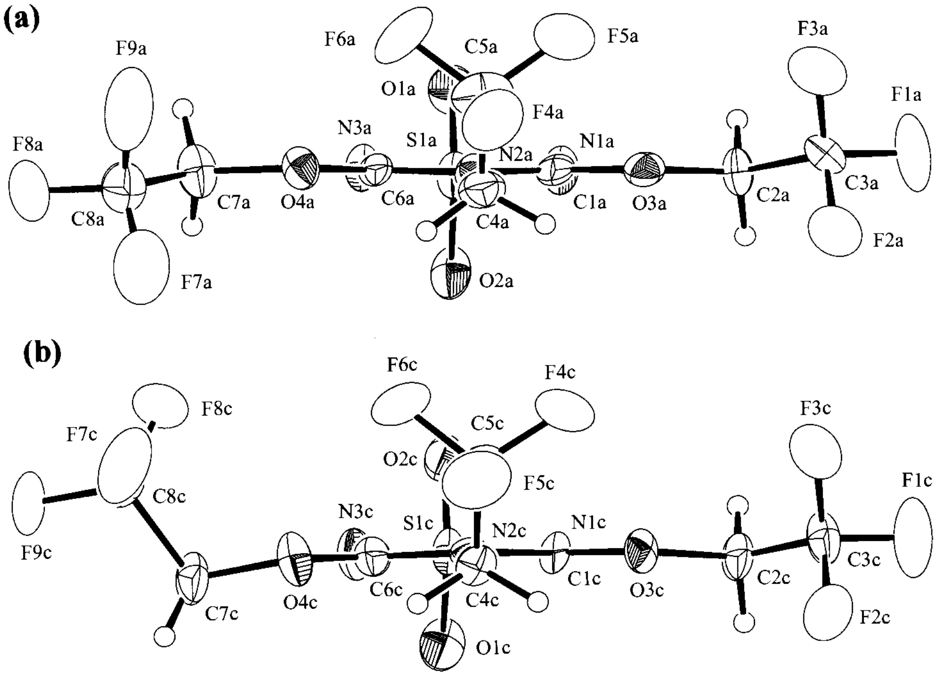
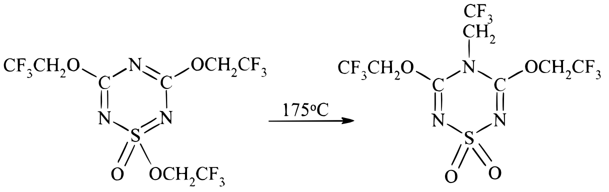


Figure 4. Views of (a) **14a** and (b) **14c** showing the different orientations of OCH_2CF_3 groups.

153−156 °C), which exhibit a molecular ion in the mass spectrum at *m*/*z* 411 suggesting that the product is an isomer of **13**. The ^{13}C NMR spectrum of this product consists of a single resonance at δ 150.7 ppm for the ring carbon atoms and two pairs of 1:3:3:1 quartets for CH_2CF_3 carbon atoms. The two quartets at δ 122.5 and δ 121.7 ppm can be attributed to CF_3 groups in different environments (cf. **13**). However, the quartets for the CH_2 carbon atoms appear at δ 66.5 and 45.3 ppm. By comparison with the NMR data for **13** the former can be attributed to $-OCH_2-$ groups, but the upfield resonance at δ 45.3 ppm implies a significantly different CH_2 environment for this CH_2CF_3 group. Thus the spectroscopic evidence suggests that the product is a symmetrical isomer of **13**.

X-ray Structure of $(CF_3CH_2O)_2(CF_3CH_2)C_2N_3SO_2$ (14). The structure of the product of the thermolysis of **13** was determined by X-ray crystallography. As indicated in Figure 3, the thermolysis of **13** promotes an O → N migration of a CH_2CF_3 group to give the sulfone **14** and the CH_2CF_3 group becomes attached to the remote (unique) nitrogen atom (eq 1).



(1)

13 **14**

The crystal structure of **14** is composed of four independent molecules in an asymmetric unit which are referred to as molecules **a**, **b**, **c**, and **d** after the letters in their atomic labels (see Figure 3). The molecular dimensions are normal and are within the range of expected values with mean bond distances S=O, 1.419(14); S−N, 1.613(13); N=C, 1.27(2); N−Csp^2, 1.380(14); N−Csp^3, 1.47(2); O−Csp^2, 1.33(2); O−Csp^3, 1.45(2); Csp^3-Csp^3, 1.49(2), and C−F, 1.32(2) Å.[30] The trends in CN bond lengths are consistent with localized π-bonding in the heterocyclic ring. Nevertheless, the geometry at N1 is essentially planar (|ΣN1 = 359.3°|). The S−N and S=O distances are similar to those reported for the $S_3N_3O_2^-$ anion.[31] Selected mean bond angles are summarized in Table 2. The SN_3C_2 rings in all the four molecules are essentially planar with molecule **a** showing the largest deviation from planarity; χ^2 value for the plane of the heterocyclic ring being 53.9. The maximum deviation of atoms from these planes is: 0.059(13), 0.034(12), 0.028(15), and 0.027(13) Å, respectively, for the molecules **a** to **d**. A comparison of the four molecules shows that the conformations of molecules **a** and **b** are similar, but different from the conformations of molecules **c** and **d** which are also identical to each other. The molecules **a** and **b** have pseudo mirror symmetry while the other two molecules are devoid of such symmetry. These differences are more obvious from a comparison of the torsion angles involving trifluoroethoxy groups (see Table 2). For instance, the torsion angle N3−C6−O4−C7 in the four molecules ranges between 3.2(22) to 11.7(21)° and the torsion angle C6−O4−C7−C8 has values 170.2(14) and 166.0(14)° for molecules **a** and **b**, respectively,

Table 2. Selected Mean Bond Angles (deg) and Selected Torsion Angles (deg) for **14a**−**d**

N(1)−C(1)−N(2)	128.5(15
N(2)−C(6)−N(3)	125.7(14)
C(1)−N(2)−C(6)	116.6(13)
C(6)−N(3)−S(1)	121.8(11)
S(1)−N(1)−C(1)	120.1(11)
N(1)−S(1)−N(3)	106.9(7)

	molecule			
	a	**b**	**c**	**d**
N1−C1−O3−C2	−1.4(19)	−8.3(19)	−3.6(20)	−1.1(21)
C1−O3−C2−C3	171.3(13)	169.9(13)	171.6(13)	177.8(15)
N3−C6−O4−C7	4.4(20)	6.4(20)	11.7(21)	3.2(22)
C6−O4−C7−C8	170.2(14)	166.0(14)	117.1(15)	−107.7(16)

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(30) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 9.5.11, pp 691−706 Table 9.

(31) Chivers, T.; Cordes, A. W.; Oakley, R. T.; Pennington, W. T. *Inorg. Chem.* **1983**, *22*, 2429.

which are different from the values [117.1(15) and −107.7(16)°, respectively] for the corresponding angle in the molecules **c** and **d**. The different orientations of OCH_2CF_3 groups for **14a** and **14c** are illustrated in Figure 4.

Conclusions

The reaction of the hybrid cyanuric−thiazyl ring $Cl_3C_2N_3S$ with sodium alkoxides or aryloxides occurs regiospecifically at sulfur and trisubstitution can be achieved without ring degradation. ROP of $Cl_3C_2N_3S$ does not proceed cleanly owing to partial elimination of volatile sulfur chlorides. The hybrid cyanuric−sulfanuric heterocycle $Cl_3C_2N_3S(O)$ is obtained as a volatile, low melting solid by oxidation of the corresponding S(VI). The trialkoxy derivative $(CF_3CH_2O)_3C_2N_3S(O)$ undergoes a novel isomerization involving CH_2CF_3 migration (O → N) upon thermolysis. Successful ROP of these hybrid CNSN rings will require mild conditions, e.g. use of halide ion acceptors. The cation $[Cl_2C_2N_3S^+][AsF_6^-]$ may be a suitable precursor.[19b]

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Supporting Information Available: An X-ray crystallographic file for **14**, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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