

Stereochemistry of Oxidation of 1,5,2,4,6,8-Dithiatetrazocines. Preparation and Crystal Structures of $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+\text{X}^-$ ($\text{X}^- = \text{PF}_6^-, \text{Cl}_3^-$) and $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2(\text{O})_2[\text{N}(\text{CF}_3)_2]_2$

René T. Boeré,^{1a} A. Wallace Cordes,^{1b} Scott L. Craig,^{1b} Richard T. Oakley,^{*1a} and Robert W. Reed^{1a}

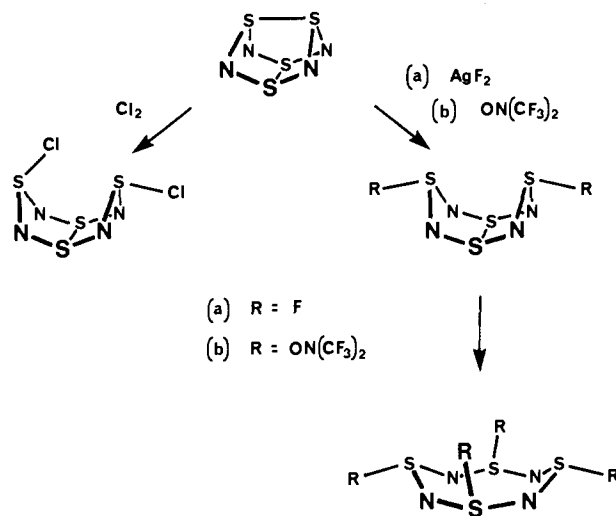
Contribution from the Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada, and Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701. Received July 10, 1986

Abstract: Structural studies on a number of oxidized derivatives of 3,7-bis(dimethylamino)-1,5,2,4,6,8-dithiatetrazocine $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2$ are reported. Oxidation with chlorine in acetonitrile yields the trichloride salt $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$, which can be converted into the corresponding $[\text{PF}_6]^-$ salt by treatment with NOPF_6 . X-ray analysis of the $[\text{PF}_6]^-$ salt reveals a crystallographically symmetric S—Cl—S bridge ($d(\text{S—Cl}) = 2.741(3) \text{ \AA}$), while in the trichloride salt the bridge is markedly asymmetric ($d(\text{S—S}) = 2.290$ and 3.225 \AA), the disposition of the cation-anion pair illustrating an incipient electrophile-nucleophile interaction. Oxidation of $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2$ with bis(trifluoromethyl) nitroxide yields (inter alia) $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2(\text{O})_2[\text{N}(\text{CF}_3)_2]_2$, X-ray structural analysis of which reveals a boat-shaped conformation for the $\text{C}_2\text{N}_4\text{S}_2$ ring with the two $\text{N}(\text{CF}_3)_2$ groups occupying equatorial sites on the same side of the ring. This geometry is suggested to arise from a stereospecific intramolecular rearrangement of the initially produced *cis*-bis(nitroxide) derivative $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2[\text{ON}(\text{CF}_3)_2]_2$. The stereochemical features of all three structures are interpreted in terms of the dominant frontier orbital interactions expected between $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2$ and free radical and polar oxidants. Crystal data for $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{PF}_6]^-$ are as follows: orthorhombic, space group *Imm*2, $a = 10.339(2) \text{ \AA}$, $b = 12.048(2) \text{ \AA}$, $c = 6.121(2) \text{ \AA}$, $Z = 2$, and $V = 762.5(5) \text{ \AA}^3$. Crystal data for $[(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2\text{Cl}]^+[\text{Cl}_3]^-$ are as follows: orthorhombic, space group *Pnma*, $a = 23.644(3) \text{ \AA}$, $b = 10.773(3) \text{ \AA}$, $c = 5.862(2) \text{ \AA}$, $Z = 4$, and $V = 1493(1) \text{ \AA}^3$. Crystal data for $(\text{Me}_2\text{N})_2\text{C}_2\text{N}_4\text{S}_2(\text{O})_2[\text{N}(\text{CF}_3)_2]_2$ are as follows: monoclinic, space group *P2*₁/*c*, $a = 8.971(2) \text{ \AA}$, $b = 11.188(2) \text{ \AA}$, $c = 20.876(9) \text{ \AA}$, $\beta = 102.20(3)^\circ$, $Z = 4$, $V = 2048(2) \text{ \AA}^3$. The final residual factors (observed reflections) were respectively 0.061 (596), 0.091 (1750), and 0.041 (1362).

The unusual molecular shapes of binary sulfur nitrides have evoked continued debate over their electronic structures. The nature of the 2.59 Å transannular S—S contacts in S_4N_4 ² has, in particular, been a source of controversy; i.e., is there a bond? By using theoretically calculated total overlap populations as the criterion for bond strength the general consensus is that the 1,5-interaction is bonding, albeit weakly, while the 1,3-interaction is not.³ On the other hand the results of a recent gradient analysis of S_4N_4 indicate that the form of the Laplacian of the charge density along the S—S coordinate more nearly resembles the closed shell interactions found between nonbonded atoms.⁴ However, from a thermodynamic viewpoint none of these conclusions provide, by themselves, much substantive information. There is no way we can measure or calculate the strength of the transannular interactions in S_4N_4 , e.g., by opening the D_{2d} cage structure into a planar D_{4h} modification and assessing the concomitant enthalpy change, since it would be impossible to extricate the S—S bond energy component from the reorganizational energy term associated with the torsional motion of the skeletal SN bonds.

Regrettably, the preoccupation with the ground-state strength of these interactions has clouded some important questions regarding chemical reactivity. That S_4N_4 can be oxidized has been known for many years, but little attention has been given to the electronic factors which might influence the thermodynamics and kinetics of these reactions (Scheme I). Recently we suggested that the stereochemistries exhibited by the products of oxidative

Scheme I



addition to S_4N_4 could be rationalized in terms of the frontier orbital interactions that guide the formation of the transition states.⁵ Accordingly the unsymmetrical geometry of $\text{S}_4\text{N}_4\text{Cl}_2$ ⁶ and the symmetrically substituted structures of $\text{S}_4\text{N}_4\text{R}_2$ ^{7,8} and $\text{S}_4\text{N}_4\text{R}_4$ ^{9,10} ($\text{R} = \text{F}, \text{ON}(\text{CF}_3)_2$) were interpreted in terms of the

(1) (a) University of Guelph. (b) University of Arkansas.

(2) (a) Sharma, B.; Donohue, J. *Acta Crystallogr.* **1963**, *16*, 891. (b) DeLucia, M. L.; Coppens, P. *Inorg. Chem.* **1978**, *17*, 2336.

(3) For example, see: (a) Chivers, T.; Fielding, L.; Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1979**, *18*, 3379. (b) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Egdel, R. G.; Evans, R. *Inorg. Chem.* **1980**, *19*, 1307. (c) Haddon, R. C.; Wudl, R.; Williams, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 6687. (d) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174.

(4) Tang, T.-H.; Bader, R. F. W.; MacDougall, P. J. *Inorg. Chem.* **1985**, *24*, 2047.

(5) Oakley, R. T. *Can. J. Chem.* **1984**, *62*, 2763.

(6) Zak, Z. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 23.

(7) Zborilova, L.; Gebaur, P. *Z. Anorg. Allg. Chem.* **1979**, *448*, 5.

(8) Mews, R. J. *Fluorine Chem.* **1981**, *18*, 155.

(9) Wieggers, G. A.; Vos, A. *Acta Crystallogr.* **1963**, *16*, 152.

(10) (a) Emelüs, H. J.; Forder, R. A.; Poulet, R. J.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1970**, 1483. (b) Emelüs, H. J.; Poulet, R. J. *J. Fluorine Chem.* **1971/72**, *1*, 13. (c) Forder, R. A.; Sheldrick, G. M. *J. Fluorine Chem.* **1971/72**, *1*, 23.

expected differences in the directions of attack of polar and free radical oxidants.

In order to test the veracity of these concepts we are now studying the reactivity patterns of other compounds which are structurally related to S_4N_4 . In the present work we describe the reactions of 3,7-bis(dimethylamino)-1,5,2,4,6,8-dithiatetrazocine $(Me_2N)_2C_2N_4S_2^{11}$ with a variety of radical and polar oxidants and discuss the molecular structures of the products in terms of the concepts developed earlier.^{5,12}

Experimental Section

Starting Materials and General Procedures. The dithiatetrazocines $R_2C_2N_4S_2$ ($R = NMe_2, Ph$)¹¹ and $Me_4P_2N_4S_2^{13}$ were prepared according to the literature methods, as were $(CF_3)_2NOH^{14}$ and $(CF_3)_2NO^{15}$. Reagent grade chlorine (Matheson), sulfonyl chloride, and nitrosyl hexafluorophosphate (Aldrich) were obtained commercially. The solvents acetonitrile and carbon tetrachloride were both purified by distillation from phosphorus pentoxide. 1H and ^{13}C NMR spectra were recorded on a Bruker WH-400, and ^{19}F NMR spectra were obtained on a Varian XL-300 spectrometer. IR spectra (Nujol mulls, CsI optics) were recorded on a Perkin-Elmer 1330 grating spectrophotometer. Mass spectra were obtained on a VG 7070 EF mass spectrometer, samples being admitted through conventional inlet systems. Chemical analyses were performed by MHW laboratories, Phoenix, AZ.

Reaction of $(Me_2N)_2C_2N_4S_2$ with Chlorine. When chlorine gas was passed over a solution of $(Me_2N)_2C_2N_4S_2$ (0.50 g, 2.2 mmol) in dry acetonitrile, the solution turned orange-red immediately. Upon cooling this solution to $-25^\circ C$ overnight small extremely moisture-sensitive orange-red crystals (ca. 100 mg) of $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$, dec $> 98^\circ C$, were obtained [1H NMR ($CDCl_3$) δ 3.34; EI (70 eV) MS, m/e (rel intensity) 266 (M^+ , 1), 232 ($M - Cl^+$, 22), 186 ($(Me_2N)_2C_2N_4S_2^+$, 24), 148 ($Me_2NCN_2S_2^+$, 21), 116 ($Me_2NCN_2S^+$, 15), 96 (? , 11), 87 (? , 100); IR (1600–250- cm^{-1} region) 1570 (vs, br), 1400 (vs, br), 1290 (vs, br), 995 (w), 940 (m), 878 (s), 735 (m), 648 (s), 465 (w), 420 (w), 390 (w), 365 (w)]. Attempts to establish the elemental composition of this material by chemical analysis were unsuccessful; rapid loss of sample weight occurred on contact of the crystals with air. The identity of the compound was eventually established by single-crystal X-ray diffraction (see below). The compound was also prepared in higher yield (93%) by the action of chlorine or excess sulfonyl chloride on $(Me_2N)_2C_2N_4S_2$ in dry carbon tetrachloride. The curdled orange precipitate so obtained exhibited the same IR, NMR, and mass spectrum as the crystalline material obtained from the chlorine/acetonitrile reaction.¹⁶

Preparation of $[(Me_2N)_2C_2N_4S_2Cl]^+[PF_6]^-$. This salt was prepared by anion exchange between $[(Me_2N)_2C_2N_4S_2Cl]^+[Cl_3]^-$ and $NOPF_6$ in hot acetonitrile. The bright red air sensitive crystals, dec $> 160^\circ C$, obtained upon cooling the solution to $-25^\circ C$ were filtered off and characterized by X-ray crystallography (see below): IR (1600–250- cm^{-1} region) 1600 (vs, br), 1400 (s br), 1310 (s), 1275 (s), 1230 (w), 1110 (vw), 1060 (w), 1005 (m), 940 (m), 895 (s), 830 (vs, br), 740 (m), 650 (s), 560 (vs), 470 (w), 425 (w), 400 (w), 370 (vw), 270 (s).

Attempted Oxidation of $Ph_2C_2N_4S_2$ with Chlorine. No visible change was noted when chlorine gas was passed over a slurry of $Ph_2C_2N_4S_2$ in acetonitrile. After 1 h the starting material was recovered unchanged from the reaction mixture.

Reaction of $(Me_2N)_2C_2N_4S_2$ with $ON(CF_3)_2$. Bis(trifluoromethyl)nitroxide (0.87 g, 5.18 mmol) was condensed into a suspension of $(Me_2N)_2C_2N_4S_2$ (0.60 g, 2.58 mmol) in 30 mL of CCl_4 in a glass reaction tube fitted with a "Rotaflo" valve. On warming to room temperature the nitroxide dissolved in the solvent, consuming at the same time the undissolved starting material. After 16 h the solvent was removed in vacuo, and the residual solids were chromatographed on a dry silica column. Elution with CH_2Cl_2 removed 0.57 g of a colorless solid containing (by

Table I. NMR Data

	4	1	2	3
		1H (δ)		
$(CH_3)_2N$	3.15	3.172	3.170	3.181
		3.197		3.184
		3.212		3.197
$(^cCH_2)$		5.411		5.339 ^a
		^{19}F (δ)		
$(^fCF_3)$			-53.54	-53.25
				-53.36
$(^eCF_3)$		-68.34		-68.65 ^b
		^{13}C (δ)		
(^aC)	38.94	38.95	38.82	38.91
(^bC)		37.18		36.61
(^dC)		87.34		85.49
(^cC)	179.95	179.70	156.58	156.47
(^eC)		180.59		158.38
(^fC)			119.04	118.82
$(^1J_{FC}, Hz)$			(269)	(270)
(^8C)		120.60		120.50
$(^1J_{FC}, Hz)$		(272)		(272)

^a AB pattern, $\delta(A) = 5.046$, $\delta(B) = 5.632$, $J_{AB} = 10.9$ Hz. ^b Line broadened, $\nu_{(1/2)} = 18$ Hz.

TLC analysis on SiO_2 two major components (A, R_f 0.57; B, R_f 0.73) and a minor fraction (C, R_f 0.80). Further elution with 90/10 $CH_2Cl_2/EtOAc$ removed unreacted $(Me_2N)_2C_2N_4S_2$ (R_f (CH_2Cl_2 , SiO_2) 0.10 (0.157 g, 0.68 mmol)) and an additional faster moving fraction (R_f (CH_2Cl_2 , SiO_2) 0.20) which was recrystallized from ether/hexane as yellow microcrystals of $[(CF_3)_2NOCH_2MeN]Me_2NC_2N_4S_2$ (**1**) (0.239 g, 0.60 mmol) [mp 106–108 $^\circ C$; EI (70 eV) MS, m/e (rel intensity) 399 (M^+ , 11), 231 ($[M - ON(CF_3)_2]^+$, 100), 188, ($[231 - CH_2NMe]^+$, 58), 148 ($[Me_2NC(NS)_2]^+$, 50)]. Anal. Calcd for $C_8H_{11}F_6N_7OS_2$: C, 24.06; H, 2.78; N, 24.55. Found: C, 24.10; H, 2.80; N, 24.56. Flash chromatography of the mixture of A, B, and C (on SiO_2 , 20–45 μ mesh) with 90/10 hexane/ $EtOAc$ as the eluting solvent afforded pure samples of the first two components. Component A, $(Me_2N)_2C_2N_4S_2(O_2)[N(CF_3)_2]_2$ (**2**), (0.388 g, 0.68 mmol) was recrystallized from ether/hexane as colorless plates, mp 138–141 $^\circ C$; EI (70 eV) MS, m/e (rel intensity) 568 (M^+ , 11), 416 ($[M - (CF_3)_2N]^+$, 31), 373 ($[416 - CH_2NMe]^+$, 100), 346 ($[416 - CF_2H]^+$, 28). Anal. Calcd for $C_{10}H_{12}F_{12}N_8O_2S_2$: C, 21.13; H, 2.13; N, 19.72; S, 11.28. Found: C, 21.58; H, 2.42%; N, 19.62; S, 11.21. Component B, $[(CF_3)_2NOCH_2MeN](Me_2N)_2C_2N_4S_2(O_2)[N(CF_3)_2]_2$ (**3**), (0.14 g, 0.19 mmol) was crystallized from ether/hexane as colorless needles, mp 131–135 $^\circ C$; EI (70 eV) $ms, m/e$ (rel intensity): 734 ($[M - H]^+$, 1), 583 ($[M - N(CF_3)_2]^+$, 5), 567 ($[M - (CF_3)_2NO]^+$, 100), 524 ($[567 - CH_2NMe]^+$, 37). Anal. Calcd for $C_{12}H_{11}F_{18}N_9O_3S_2$: C, 19.60; H, 1.51; N, 17.14; S, 8.72. Found: C, 19.46; H, 1.68; N, 17.15; S, 8.79. Component C (40 mg) was identified as $c-S_8$ by mass spectrometry. 1H , ^{13}C , and ^{19}F NMR parameters for **1**, **2**, and **3** are given in Table I.

Attempted Oxidation of $Ph_2C_2N_4S_2$ and $Me_4P_2N_4S_2$ with $(CF_3)_2NO$. Both of these compounds failed to react after prolonged exposure, in solution or neat, with excess $(CF_3)_2NO$.

X-ray Structural Analyses. Crystals of $[(Me_2N)_2C_2N_4S_2Cl]^+X^-$ ($X^- = Cl_3^-$ and PF_6^-) suitable for X-ray work were obtained directly from the reaction mixtures (see above) in acetonitrile and were mounted under a nitrogen atmosphere in glass capillaries. Data sets on each salt were collected from three different crystals, because of uniformly poor quality of the trichloride crystals and for independent checks of the anion disorder (vide infra) in the fluorophosphate salt. While the final R factor reported here for the trichloride is higher than normal, the standard deviations are sufficient for the structural arguments being presented. Crystals of $(Me_2N)_2C_2N_4S_2(O_2)[N(CF_3)_2]_2$ (**2**) were grown from a diethyl ether/hexane mixture and mounted on glass fibers. Data collection and refinement parameters are listed in Table II. Data collection procedures and computational methods used were as previously described.¹⁸

(17) (a) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 447. (b) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 47.

(11) Ernst, I.; Holick, W.; Rihs, G.; Schomburg, D.; Shohain, G.; Wenkert, D.; Woodward, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1540.

(12) For a preliminary account of part of this work, see: Boerē, R. T.; Cordes, A. W.; Oakley, R. T.; Reed, R. W. *J. Chem. Soc., Chem. Commun.* **1985**, 655.

(13) Burford, N.; Chivers, T.; Codding, P. W.; Oakley, R. T. *Inorg. Chem.* **1982**, *21*, 982.

(14) Makarov, S. P.; Yakubovlch, A. Ya; Dubov, S. S.; Medvedev. *Akad. Nauk. SSSR Doklady Chem.* **1965**, *160*, 1319.

(15) Ang, H. G. *J. Chem. Soc., Chem. Commun.* **1968**, 1320.

(16) At approximately the same time as our original communication (ref 12) another paper reporting the same reaction appeared in press (ref 17a). In a private communication Professor Chivers has suggested that the product described by his group as 1,5- $(Me_2NCN)_2(NSCl)_2$ is in fact the salt $[(Me_2N)_2C_2N_4S_2Cl]^+Cl^-$. We agree. We note, however, that the 1H NMR chemical shift for 1,5- $(Me_2NCN)_2(NSCl)_2$ in ref 17b is in error. The correct value is δ 3.30.

Table II. Crystal Data

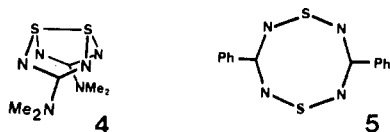
	$C_6H_{12}N_6S_2Cl_4$	$C_6H_{12}N_6S_2ClPF_6$	$C_{10}H_{12}N_8S_2O_2F_{12}$
formula	$C_6H_{12}N_6S_2Cl_4$	$C_6H_{12}N_6S_2ClPF_6$	$C_{10}H_{12}N_8S_2O_2F_{12}$
formula wt	374.1	412.7	568.4
F_{000}	760	416	1136
cryst syst	orthorhombic	orthorhombic	monoclinic
space grp; mols/cell	$Pnma$; 4	$Imm2$; 2	$P2_1/c$; 4
site symmetry	$m (C_s)$	$m (C_{2v})$	$1 (C_1)$
$a, \text{Å}$	23.644 (3)	10.339 (2)	8.971 (2)
$b, \text{Å}$	10.773 (3)	12.048 (2)	11.188 (2)
$c, \text{Å}$	5.862 (2)	6.121 (2)	20.876 (9)
β, deg			120.20 (3)
$V, \text{Å}^3$	1493 (1)	762.5 (5)	2048 (2)
$D_{\text{calcd}}, \text{g cm}^{-3}$	1.66	1.80	1.84
2θ range for cell detn. (deg)	24–37	22–27	20–23
reflens scanned; obsd	1563; 750	977; 569	3594; 2232
$2\theta_{\text{max}}, \text{deg}$	50	70	50
decay correctn range	0.98–1.00	0.97–1.00	none
cryst size, mm	$0.30 \times 0.30 \times 0.50$	$0.28 \times 0.34 \times 0.64$	$0.14 \times 0.48 \times 0.50$
μ (Mo $K\alpha$), cm^{-1}	10.58	6.81	3.80
absn correctn range	0.66–1.00	0.92–1.00	0.89–1.00
H atom treatment	refd isotropically	diff map pos	idealized
params refined	91	71	355
final R ; R_w	0.091; 0.140	0.061; 0.078	0.041; 0.055
max peak final diff map ($e \text{Å}^{-3}$)	1.74 (3)	0.54 (3)	0.30 (3)
weighting factor ρ	0.05	0.06	0.06

The PF_6^- anion in $[(Me_2N)_2C_2N_4S_2Cl]^+[PF_6^-]$ is disordered and was modelled by a multitude of F atoms constrained to positions suggested by difference maps. Multiplicities were refined at the isotropic level of refinement; F atoms with multiplicities >0.12 were then refined anisotropically. Atom coordinates for all three structures are provided in Table III, while selected bond distance and angle information is presented in Table IV.

Theoretical Calculations. One-electron orbital energies and distributions for H_2S_2 , S_4N_4 , and $(NH_2)_2C_2N_4S_2$ derivatives were obtained from the MNDO²¹ program of Dewar and Thiel.

Results and Discussion

Frontier Orbitals of Dithiatetrazocines. The structural dichotomy¹¹ that exists between the structures of $(Me_2N)_2C_2N_4S_2$ (**4**) and $Ph_2C_2N_4S_2$ (**5**) has been the subject of several recent theoretical studies.^{5,20–22} To the extent that there is any bonding



interaction between the transannular sulfur atoms in **4** the major orbital contributor to this "bond" is the diffuse HOMO illustrated in Figure 1. The LUMO represents its antibonding counterpart. However, while it is appealing to equate these orbitals with the σ and σ^* combinations of a disulfide linkage, the analogy is somewhat misleading; their structural and chemical roles are very different. The HOMO and LUMO of **4** are diffuse distributions which, in addition to possessing bonding and antibonding properties with respect to the S—S contact, also exhibit local π^* character with respect to the S—N linkages. Their one-electron energies are also different from the σ and σ^* combinations of a simple disulfide, e.g., H_2S_2 (Table V). In an organic sense the S—S σ -orbital of the model compound $(NH_2)_2C_2N_4S_2$ is more electron rich (more easily ionized) than that of a disulfide, or S_4N_4 , which, by virtue of its electronegative core, has a relatively high ionization potential.^{3b} Reciprocally, $(H_2N)_2C_2N_4S_2$ is a much better acceptor than H_2S_2 , although not quite as good as S_4N_4 . The LUMO

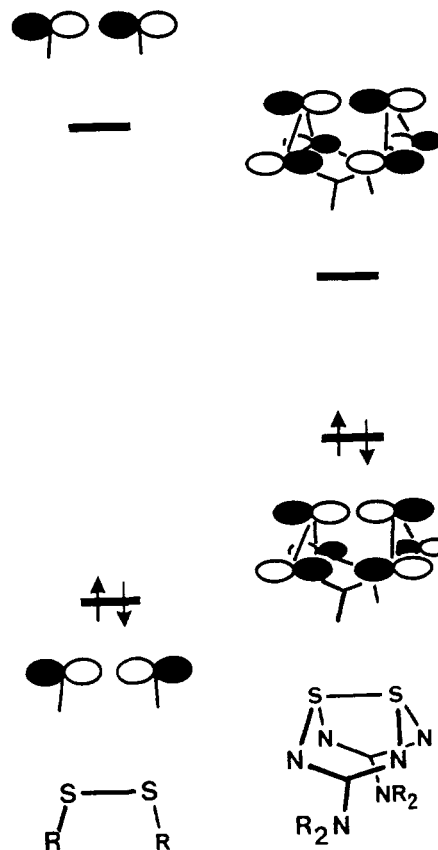


Figure 1. Qualitative representations of the S—S σ and σ^* orbitals of H_2S_2 and $(NH_2)_2C_2N_4S_2$.

energies given in Table V substantiate this interpretation, as do the relative reactivities of $(Me_2N)_2C_2N_4S_2$ and S_4N_4 (vide infra) with oxidants.

This simple orbital description of the S—S interaction of **4** provides a useful conceptual framework with which to explore the chemistry of $(Me_2N)_2C_2N_4S_2$ and related heterocycles. As in the case of S_4N_4 their reactivity toward electrophilic and nucleophilic oxidants should be interpretable with the same frontier orbital arguments used in organic chemistry.²³ Toward this end we note

(18) Cordes, A. W.; Hojo, M.; Koenig, H.; Noble, M. C.; Oakley, R. T.; Pennington, W. T. *Inorg. Chem.* **1986**, *25*, 1137.

(19) (a) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Stewart, J. P. *QCPE* **1984**, No. 455, MOPAC.

(20) Millefiori, S.; Millefiori, A. *Inorg. Chim. Acta* **1984**, *90*, L55.

(21) Boutique, J. P.; Riga, J.; Verbist, J. J.; Delhalle, J.; Fripiat, J. G.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1984**, *102*, 312.

(22) Gleiter, R.; Bartetzko, R.; Cremer, D. *J. Am. Chem. Soc.* **1984**, *106*, 3437.

(23) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: 1976.

Table III. Non-Hydrogen Atom Coordinates and Their Estimated Standard Deviations^a

atom	x	y	z	B (Å ²)
[(Me ₂ N) ₂ C ₂ N ₄ S ₂ Cl] ⁺ [Cl ₃] ⁻				
Cl(1)	0.6356 (2)	0.250	1.0852 (8)	4.6 (1)
Cl(2)	0.2857 (2)	0.250	0.2113 (9)	5.2 (1)
Cl(3)	0.3780 (2)	0.250	0.2155 (7)	3.6 (1)
Cl(4)	0.4792 (2)	0.250	0.204 (1)	6.1 (2)
S(1)	0.6918 (2)	0.250	0.7670 (7)	2.67 (8)
S(2)	0.5461 (2)	0.250	0.6701 (9)	3.6 (1)
N(1)	0.6759 (4)	0.372 (1)	0.647 (2)	3.7 (2)
N(2)	0.5741 (4)	0.3737 (9)	0.622 (2)	2.9 (2)
N(3)	0.6287 (4)	0.4943 (9)	0.396 (2)	3.1 (2)
C(1)	0.6264 (5)	0.410 (1)	0.549 (2)	2.9 (3)
C(2)	0.5764 (5)	0.546 (1)	0.286 (3)	4.2 (3)
C(3)	0.6829 (6)	0.539 (1)	0.297 (2)	4.7 (3)
[(Me ₂ N) ₂ C ₂ N ₄ S ₂ Cl] ⁺ [PF ₆] ⁻				
S	0.3333 (2)	0.000	0.5584 (5)	5.65 (4)
Cl	0.500	0.000	0.2102 (7)	7.7 (1)
P	0.000	0.000	0.000	3.87 (5)
N(1)	0.3828 (3)	0.1106 (3)	0.6469 (8)	3.22 (7)
N(2)	0.500	0.2148 (4)	0.888 (1)	2.53 (8)
C(1)	0.500	0.1415 (4)	0.735 (1)	2.4 (1)
C(2)	0.3776 (5)	0.2582 (4)	0.978 (1)	4.1 (1)
(Me ₂ N) ₂ C ₂ N ₄ S ₂ (O) ₂ [N(CF ₃) ₂] ₂				
S(1)	0.8360 (1)	0.14256 (8)	0.25262 (4)	2.59 (2)
S(2)	0.6571 (1)	0.18136 (9)	0.10081 (5)	2.74 (2)
C(1)	0.9399 (4)	0.1585 (3)	0.1487 (2)	2.84 (8)
C(2)	0.6382 (4)	0.2981 (3)	0.2023 (2)	2.76 (8)
C(3)	0.9935 (5)	0.3011 (4)	0.3416 (2)	4.5 (1)
C(4)	1.0174 (5)	0.0895 (4)	0.3689 (2)	4.5 (1)
C(5)	1.2099 (5)	0.1956 (6)	0.1719 (3)	5.9 (1)
C(6)	1.0759 (5)	0.1325 (5)	0.0601 (2)	5.4 (1)
C(7)	0.7075 (5)	0.3296 (4)	0.0026 (2)	4.1 (1)
C(8)	0.4615 (5)	0.2307 (4)	-0.0132 (2)	4.7 (1)
C(9)	0.5018 (5)	0.4837 (4)	0.1753 (2)	5.2 (1)
C(10)	0.5435 (6)	0.3968 (5)	0.2888 (2)	5.3 (1)
F(3A)	0.9180 (3)	0.3751 (2)	0.2976 (1)	4.70 (6)
F(3B)	0.9791 (4)	0.3406 (3)	0.3996 (1)	7.40 (9)
F(3C)	1.1402 (3)	0.3081 (3)	0.3391 (2)	6.65 (8)
F(4A)	1.0972 (3)	0.1345 (3)	0.4245 (1)	6.61 (8)
F(4B)	0.9249 (3)	0.0085 (2)	0.3852 (1)	5.83 (7)
F(4C)	1.1138 (3)	0.0340 (3)	0.3397 (2)	6.73 (8)
F(7A)	0.7349 (4)	0.3100 (3)	-0.0556 (1)	7.51 (8)
F(7B)	0.6417 (4)	0.4351 (3)	0.0013 (2)	6.97 (8)
F(7C)	0.8397 (3)	0.3368 (2)	0.0443 (1)	4.92 (6)
F(8A)	0.3685 (3)	0.2861 (3)	0.0195 (2)	6.29 (8)
F(8B)	0.4115 (4)	0.1222 (3)	-0.0235 (2)	7.64 (9)
F(8C)	0.4465 (4)	0.2849 (3)	-0.0707 (1)	7.33 (8)
O(1)	0.8200 (3)	0.0174 (2)	0.2579 (1)	3.50 (6)
O(2)	0.5355 (3)	0.1005 (3)	0.1012 (1)	3.85 (6)
N(1)	0.9503 (3)	0.1889 (3)	0.2116 (1)	2.93 (6)
N(2)	0.812 (3)	0.1197 (3)	0.1063 (2)	3.29 (7)
N(3)	0.6552 (3)	0.3001 (3)	0.1392 (1)	2.86 (6)
N(4)	0.6837 (3)	0.2085 (3)	0.2454 (2)	3.10 (7)
N(5)	0.9343 (3)	0.1826 (3)	0.3302 (2)	3.05 (7)
N(6)	1.0688 (4)	0.1607 (3)	0.1277 (2)	3.80 (8)
N(7)	0.6168 (3)	0.2350 (3)	0.0211 (2)	3.27 (7)
N(8)	0.5666 (4)	0.3890 (3)	0.2217 (2)	3.60 (7)

^aStarred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab^*(\cos \gamma)B(1,2) + ac^*(\cos \beta)B(1,3) + bc^*(\cos \alpha)B(2,3)]$.

that the phase properties and one-electron energies of the σ/σ^* orbitals of (H₂N)₂C₂N₄S₂ suggest a direct isolobal analogy with the π/π^* levels of a simple olefin (an electron deficient one at that). In the following section we describe chemical and structural results pertaining to these ideas.

Polar Oxidation of Dithiatetrazocines. The dithiatetrazocine **4** reacts rapidly (far more so than S₄N₄) with a wide range of chlorinating agents, including chlorine itself, sulfuryl chloride, and iodobenzene dichloride, to give the bright orange, extremely moisture sensitive trichloride salt [(Me₂N)₂C₂N₄S₂Cl]⁺[Cl₃]⁻; anion exchange of this salt with NOPF₆ affords the corresponding hexafluorophosphate salt [(Me₂N)₂C₂N₄S₂Cl]⁺[PF₆]⁻. X-ray

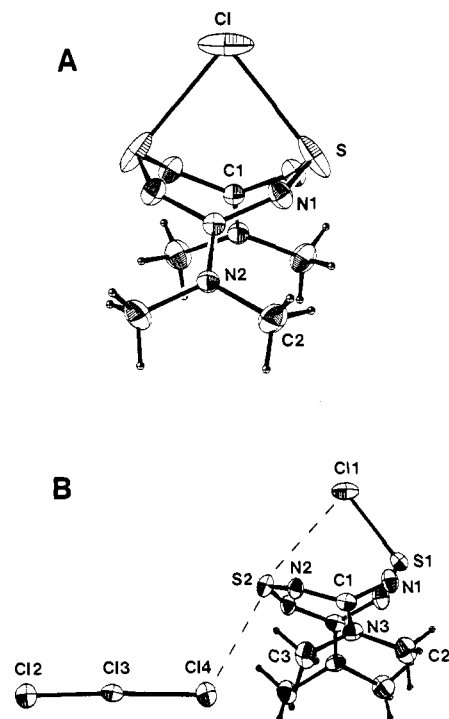


Figure 2. ORTEP drawings of the [(Me₂N)₂C₂N₄S₂Cl]⁺ cation in its (A) [PF₆]⁻ and (B) [Cl₃]⁻ salts. In the latter the disposition of the anion is also shown.

structural results on both these salts are outlined below.

ORTEP drawings of the [(Me₂N)₂C₂N₄S₂Cl]⁺ cations in the [PF₆]⁻ and [Cl₃]⁻ salts are shown in Figure 2. For the latter the disposition of the cation-anion pair is also illustrated. Pertinent bond length and angle information for both structures is provided in Table IV. Crystals of the [PF₆]⁻ salt consist of discrete ions in which the cation and anion both lie on two mutually perpendicular crystallographic mirror planes. As a result of this fortuitous feature, the single chlorine atom straddles the S—S vector in a perfectly symmetrical fashion. The single S—Cl distance (2.741 Å) is somewhat shorter than that found for the intermolecular S—Cl bridge in S₄N₅Cl (2.811 Å).^{3a} In the trichloride salt the eight-membered C₂N₄S₂ ring of the cation is bisected by a single crystallographic mirror plane which also contains the trichloride anion. The bridging S—Cl—S unit is now markedly asymmetric, although the S—S separation (3.491 Å) is similar to that found in the [PF₆]⁻ salt (3.38 Å). However a comparison of the S—Cl—S unit in the [Cl₃]⁻ salt with the corresponding moiety in the [Zr₂Cl₁₀]²⁻ and [FeCl₄]⁻ salts^{24,25} of the [S₄N₄Cl]⁺ cation (Table VI) reveals that some secondary S—Cl interaction is still maintained. Thus, while the short and long S—Cl contacts in these latter structures are nearly identical with those found in S₄N₄Cl₂, those in [(Me₂N)₂C₂N₄S₂Cl]⁺[Cl₃]⁻ suggest a slight strengthening of the secondary (longer) bond at the expense of the primary (shorter). The dihedral angles between the two five-atom CN₂S₂ mean planes [(Cl₃]⁻, 126°; [PF₆]⁻, 123°) are larger than in the unoxidized compound (101°), the increase reflecting the changing hybridization at sulfur. The mean S—N bonds in the cations are markedly shorter than in the unoxidized compound (1.605 Å), while the endocyclic CN bonds and exocyclic ligand geometries remain virtually unchanged.

The pronounced asymmetry of the S—Cl—S unit in the [Cl₃]⁻ salt compared to that found in the [PF₆]⁻ salt can be related to the effects of secondary interactions with the anion. The Cl₃⁻ ion lies under the fold of the C₂N₄S₂ ring opposite the bridging Cl1 atom. The three atom sequence is almost linear (177.7°) but

(24) Demant, U.; Conradi, E.; Pebler, J.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *515*, 69.

(25) Eicher, J.; Mueller, U.; Dehnicke, K.; *Z. Anorg. Allg. Chem.* **1985**, *521*, 37.

Table IV. Selected Structural Parameters and Their Estimated Standard Deviations

atom 1	atom 2	distance	atom 1	atom 2	atom 3	angle
[(Me ₂ N) ₂ C ₂ N ₄ SCl] ⁺ [Cl ₃] ⁻						
Cl(1)	S(1)	2.290 (3)	Cl(2)	Cl(3)	Cl(4)	177.7 (2)
Cl(2)	Cl(3)	2.183 (4)	Cl(1)	S(1)	N(1)	103.4 (2)
Cl(3)	Cl(4)	2.393 (4)	N(1)	S(1)	N(1)	117.5 (4)
S(1)	N(1)	1.542 (6)	N(2)	S(2)	N(2)	123.3 (4)
S(2)	N(2)	1.514 (5)	S(1)	N(1)	C(1)	131.0 (5)
N(1)	N(2)	2.411 (7)	S(2)	N(2)	C(1)	135.0 (4)
N(1)	C(1)	1.363 (7)	C(1)	N(3)	C(2)	122.0 (5)
N(2)	C(1)	1.366 (7)	C(1)	N(3)	C(3)	122.7 (5)
N(3)	C(1)	1.277 (7)	C(2)	N(3)	C(3)	115.0 (5)
N(3)	C(2)	1.501 (7)				
N(3)	C(3)	1.487 (8)				
[(Me ₂ N) ₂ C ₂ N ₄ SCl] ⁺ [PF ₆] ⁻						
S	Cl	2.741 (3)	S	Cl	S	77.9 (1)
S	N(1)	1.527 (3)	N(1)	S	N(1)	121.5 (3)
N(1)	C(1)	1.377 (4)	N(1)	S	Cl	93.7 (2)
C(1)	N(2)	1.285 (6)	S	N(1)	C(1)	132.1 (3)
N(2)	C(2)	1.477 (4)	N(1)	C(1)	N(1)	123.2 (4)
			N(1)	C(1)	N(2)	118.1 (2)
			C(1)	N(2)	C(2)	121.1 (2)
			C(2)	N(2)	C(2)	117.9 (5)
(Me ₂ N) ₂ C ₂ N ₄ S ₂ (O) ₂ [N(CF ₃) ₂] ₂						
S(1)	N(1)	1.557 (3)	N(1)	S(1)	N(4)	117.6 (2)
S(1)	N(4)	1.532 (3)	N(1)	S(1)	N(5)	99.4 (2)
S(1)	N(5)	1.731 (3)	N(1)	S(1)	O(1)	117.5 (2)
S(1)	O(1)	1.414 (2)	N(4)	S(1)	N(5)	103.5 (2)
S(2)	N(2)	1.538 (3)	N(4)	S(1)	O(1)	112.4 (2)
S(2)	N(3)	1.553 (3)	N(5)	S(1)	O(1)	102.9 (2)
S(2)	N(7)	1.734 (3)	N(2)	S(2)	N(3)	117.0 (2)
S(2)	O(2)	1.419 (3)	N(2)	S(2)	N(7)	103.2 (2)
C(1)	N(1)	1.342 (4)	N(2)	S(2)	O(2)	113.6 (2)
C(1)	N(2)	1.360 (5)	N(3)	S(2)	N(7)	100.2 (2)
C(1)	N(6)	1.320 (4)	N(3)	S(2)	O(2)	116.7 (2)
C(2)	N(3)	1.357 (4)	N(7)	S(2)	O(2)	102.8 (2)
C(2)	N(4)	1.352 (4)	S(1)	N(1)	C(1)	122.4 (2)
C(2)	N(8)	1.313 (4)	S(1)	N(4)	C(2)	124.0 (2)
N-C(Me)	range	1.454-1.469	S(2)	N(2)	C(1)	121.9 (2)
	av	1.461	S(2)	N(3)	C(2)	120.2 (2)
N-C(CF ₃)	range	1.426-1.436	N(1)	C(1)	N(2)	126.4 (3)
	av	1.430	N(3)	C(2)	N(4)	125.4 (3)
			C(3)	N(5)	C(4)	116.8 (3)
C-F	range	1.296-1.338	C(5)	N(6)	C(6)	117.5 (4)
	av	1.319	C(7)	N(7)	C(8)	116.0 (3)
			C(9)	N(8)	C(10)	118.2 (4)
C-H	range	0.81-1.08	S(1)	N(5)	C(3)	119.6 (3)
	av	0.92	S(1)	N(5)	C(4)	116.3 (3)
			S(2)	N(7)	C(7)	119.9 (2)
			S(2)	N(7)	C(8)	117.0 (3)
				N-C-N(exo)	range	115.8-117.8
					av	117.0
				C-N-C(Me)	range	120.0-122.5
					av	121.1
				N-C-F	range	109.8-113.4
					av	111.5
				F-C-F	range	106.7-108.3
					av	107.4

Table V. MNDO S-S σ/σ^* -Orbital Energies (eV)

orbital	H ₂ S ₂	S ₄ N ₄	(NH ₂) ₂ C ₂ N ₄ S ₂
S-S σ^*	-0.43	-2.86	-2.61
S-S σ	-13.66	-10.76	-8.51

Table VI. S--Cl--S Parameters (in Å) in Selected Compounds

compound	S-Cl	S--Cl	S--S	ref
(Me ₂ N) ₂ C ₂ N ₄ S ₂			2.428	11
[(Me ₂ N) ₂ C ₂ N ₄ S ₂ Cl] ⁺ [Cl ₃] ⁻	2.290	3.225	3.491	<i>a</i>
[(Me ₂ N) ₂ C ₂ N ₄ S ₂ Cl] ⁺ [PF ₆] ⁻	2.71	2.71	3.38	<i>a</i>
S ₄ N ₄			2.59	2
S ₂ N ₄ Cl ₂	2.179	3.488	3.859	6
[S ₄ N ₄ Cl] ⁺ [FeCl ₄] ⁻	2.139	3.501	4.001	24
2[S ₄ N ₄ Cl] ⁺ [Zr ₂ Cl ₁₀] ²⁻	2.129 ^b	3.575 ^b	4.013 ^b	25

^aThis work. ^bAverage from two cations.**Table VII.** Bond Lengths (Å) in Trichloride Structures

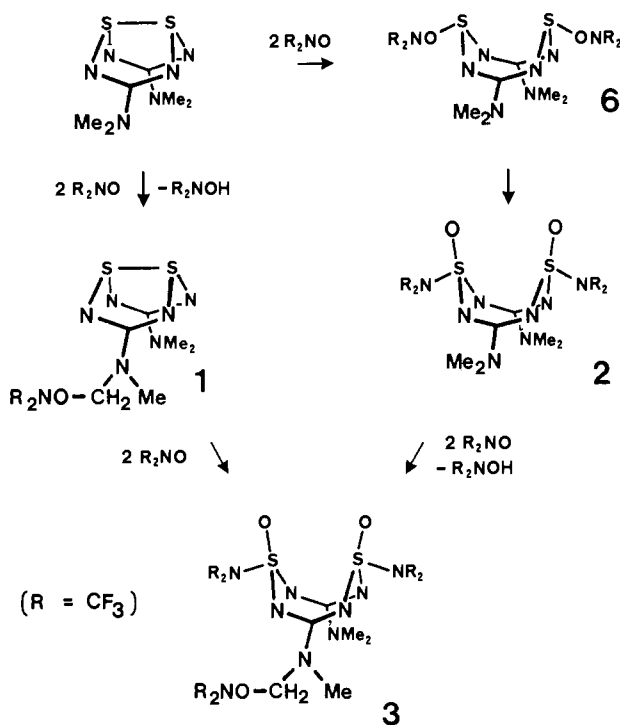
compound	Cl _a -Cl _b	Cl _b -Cl _c	ref
[(Me ₂ N) ₂ C ₂ N ₄ S ₂ Cl] ⁺ [Cl ₃] ⁻	2.393	2.183	this work
[Ph ₄ As] ⁺ [Cl ₃] ⁻	2.305	2.227	27
[(Me ₂ NC(Cl)N) ₂ SCl] ⁺ [Cl ₃] ⁻	2.340	2.249	26

markedly asymmetric in comparison to the two other reported trichloride structures (see Table VII).^{26,27} Consistently with the normal MO description of a trihalide anion the two Cl-Cl bond lengths vary inversely from structure to structure, the values found in the present case suggesting a considerable weakening of the

(26) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1985**, *24*, 2453.

(27) Bogaard, M. P.; Peterson, J.; Rae, A. D. *Acta Crystallogr.* **1981**, *37*, 1357.

Scheme II



Cl4–Cl3 bond relative to the Cl3–Cl2. Concomitant with the weakening of the trichloride unit is the development of a cation–anion interaction between Cl4 and S2 (3.160 Å), the direction of approach being approximately trans (C11–S2–Cl4 = 169.1°) to the bridging Cl1 atom. The S2–Cl4–C3 angle is 70.7°.

Radical Oxidation of Dithiatetrazocines. In contrast to S₄N₄, (Me₂N)₂C₂N₄S₂ is relatively inert to radical attack; it fails to react with AgF₂, (*t*-BuO)₂, or (PhC(O)O)₂. However, it does react with the highly nucleophilic radical (CF₃)₂NO, although the corresponding phosphorus derivative Me₄P₂N₄S₂ does not. Perhaps predictably the reaction is far less specific than the corresponding reaction with S₄N₄.^{8,10} We have isolated three products, two of which possess an exocyclic –CH₂ON(CF₃)₂ unit formed, presumably, by radical attack at a methyl group, abstraction of a hydrogen atom to produce (CF₃)₂NOH, and subsequent uptake of a second molecule of (CF₃)₂NO. The overall reaction sequence is summarized in Scheme II. The major product is an air stable colorless crystalline solid with the apparent composition (Me₂N)₂C₂N₄S₂[ON(CF₃)₂]₂. Somewhat to our surprise, subsequent single-crystal X-ray analysis revealed not the expected structure **6** but the rearranged configuration **2**. The structures of **1** and **3** have been assigned on the basis of the ¹H, ¹⁹F, and ¹³C NMR spectra and their mass spectra (Table I).²⁸

ORTEP drawings of (Me₂N)₂C₂N₄S₂(O)₂[N(CF₃)₂]₂ are shown in Figure 3. The eight-membered C₂N₄S₂ ring adopts a boatlike conformation, the N1–S1–N4–C2 and C1–N2–S2–N3 planes

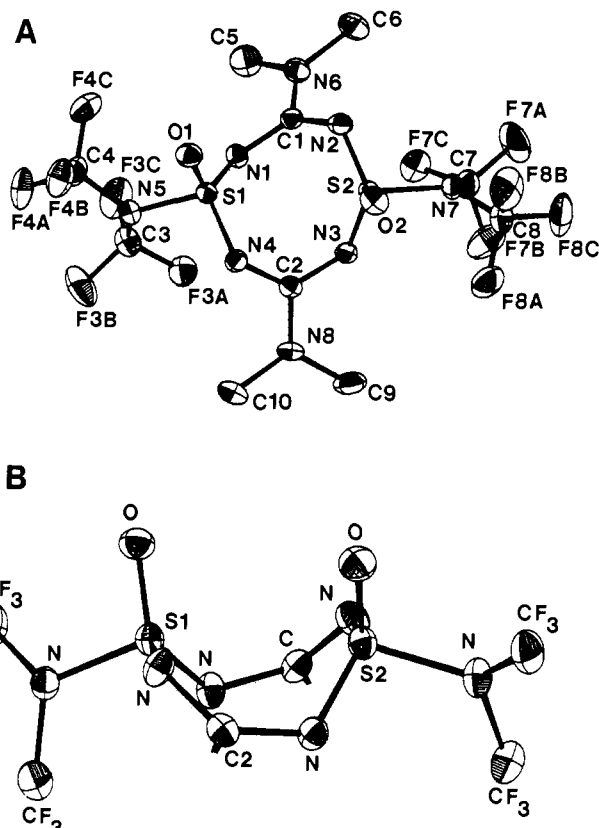


Figure 3. ORTEP drawings of (Me₂N)₂C₂N₄S₂(O)₂[N(CF₃)₂]₂, showing (A) the atom numbering scheme and (B) the ring conformation and the orientation pattern of the ligands.

making dihedral angles of 133.7 and 130.5°, respectively, with the C1–N1–C2–N3 plane. The two N(CF₃)₂ groups occupy pseudo-equatorial positions while the two oxygen atoms take up axial sites. The endocyclic C–N bonds are, on average (1.353 Å), marginally longer than in the parent compound (1.348 Å). The endocyclic S–N bonds fall into two groups each of which is substantially shorter than in (Me₂N)₂C₂N₄S₂ (1.605 Å). The sum of the bond angles at N5 and N7 is 352.7 and 352.8°, respectively, suggesting substantial ligand/ring π-bonding. However, contrary to expectation, the exocyclic S–N bonds are surprisingly long.

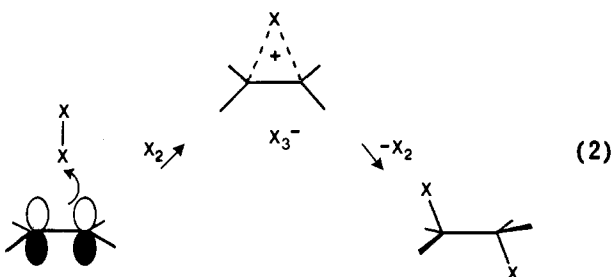
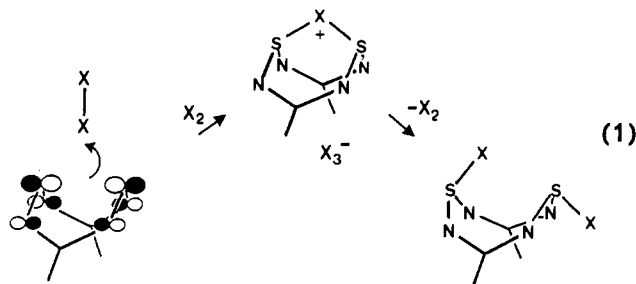
In contrast to the relative reactivity of (Me₂N)₂C₂N₄S₂ (**4**), its phenyl-substituted analogue Ph₂C₂N₄S₂ (**5**) is completely inert; we have been unable to induce oxidation by any of the radical or polar oxidants used above. Evidently the planar 10-electron π-system of the latter is sufficiently robust to resist addition reactions.

Mechanistic Interpretation. In studying the oxidation chemistry of **4** we have sought both structural and chemical evidence in support of our earlier arguments concerning the stereochemistry of oxidation of S₄N₄. In particular we hoped to establish the viability of a (S–X–S)⁺ bridged intermediate (X = a halogen) of the type shown in eq 1; such a species would be formally analogous to the triangular halocarbanion ions implicated in the polar oxidation of olefins (eq 2).²⁹ As in polar additions to olefins, subsequent approach of a nucleophile to the bridged S–X–S structure should be directed trans to the bridging atom. The geometry of S₄N₄Cl₆⁶ is certainly consistent with this mechanism, as is the structure of the product of bromination of Ph₄P₂N₄S₂.³⁰

The structural data on the [PF₆][–] and [Cl₃][–] salts of the [(Me₂N)₂C₂N₄S₂Cl]⁺ cation find an appealing interpretation within this context. First we note that, in the absence of any cation–anion pairing, as would be the case in the [PF₆][–] salt, and with favorable lattice conditions, the perfectly symmetrical bridged cation appears to be a stable structure. When a more nucleophilic

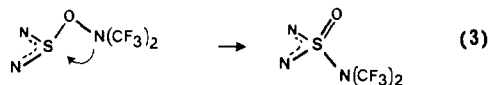
(28) The ¹⁹F spectra of **2** and **3** have sharp singlets around –53 ppm, in the normal range for (CF₃)₂NX derivatives (–51 to –58 ppm, see: compilations in *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Vol. 1, 3, 5A, 6B; Webb, G. A., Ed.; Vol. 10B and 14. **3** displays an additional line-broadened singlet around –68 ppm and **1** a sharp singlet in the same region, which is normal for (CF₃)₂NO bound to carbon. In **1** the CH₂ protons are equivalent, but in **3** they are not; the chemical shifts are those expected for a halogen-substituted methyl group. Confirmation of the structural assignments is obtained from the ¹³C spectra. The endocyclic carbon atoms in **2** and **3** are shielded by almost 24 ppm with respect to those in **1** and **4** itself. These carbons, therefore, represent a sensitive indicator of the oxidation state at the β sulfur atoms. Use of intensities and comparison between **1**, **2**, and **3** allowed assignment of all the ¹³C resonances as shown in Table I. Although the mass spectra are entirely consistent with the structures of the three products, they were of little help in assignment. If an excess of (CF₃)₂NO is used in the reaction, little or no **1** is produced; instead an additional compound, tentatively assigned as [(CF₃)₂NOCH₂NMe]₂C₂N₄S₂(O)₂[N(CF₃)₂]₂ on the basis of ¹⁹F NMR evidence, is obtained. This is presumably formed by further hydrogen abstraction from the methyl groups of **3**.

(29) (a) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504. (b) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426.



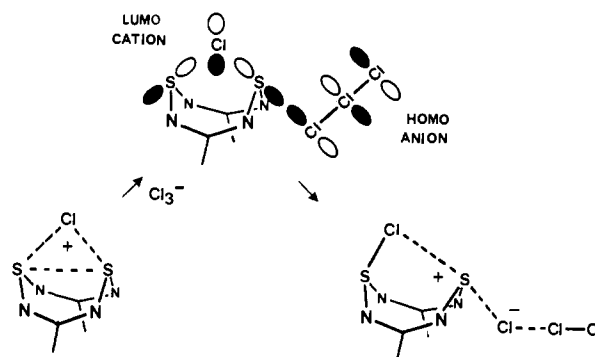
anion is introduced, more extensive cation-anion interactions can be expected. In the convention of Burgi and Dunitz³¹ the series of bond length changes in the cation and anion of the trichloride salt, the direction of approach of the anion (trans to the bridging chlorine), and the orientation of the anion (approaching sideways on to the cation) all illustrate the incipient nucleophilic attack of a solvated chloride ion on a bridged (S-Cl-S)⁺ cation. Scheme III illustrates the dominant frontier orbital interactions in this process, the π^* -HOMO of the trichloride guiding the side-on approach of the anion into the S-Cl σ^* -LUMO. The fact that the reaction is "frozen" at this point rather than proceeding through to a covalent product, as in the oxidation of S₄N₄ and Ph₄P₂N₄S₂,³⁰ is probably a result of the smaller size of the C₂N₄S₂ ring and the consequently greater transannular Cl-S interaction in the [(Me₂N)₂C₂N₄S₂Cl]⁺ cation (vide supra); in essence the transannular S-Cl contact blocks the final stage of the nucleophilic attack of the [Cl₃]⁻ anion on the cation.

In the case of the oxidation of **4** with ON(CF₃)₂ we have been unable to isolate the desired bis(nitroxide) **6** because of its rapid and irreversible isomerization to **2** at room temperature in CCl₄ (Scheme II). Such an Arbusov-like rearrangement is not without precedent. F₂PON(CF₃)₂ (δ (¹⁹F) = -67.4), for example, slowly isomerizes³² to F₂P(O)N(CF₃)₂ (δ (¹⁹F) = -54.8)³³ at 25 °C. Similarly CF₃S(O)ON(CF₃)₂ (δ (¹⁹F) = -66.8) has been reported to convert to CF₃S(O)N(CF₃)₂ (although the product was not well-characterized).³⁴ The relationship between the structure of **2** and the mechanism for radical addition to **4** then depends on whether the \equiv SON(CF₃)₂ to \equiv S(O)N(CF₃)₂ rearrangement is intramolecular and, hence, stereospecific (eq 3). That this is



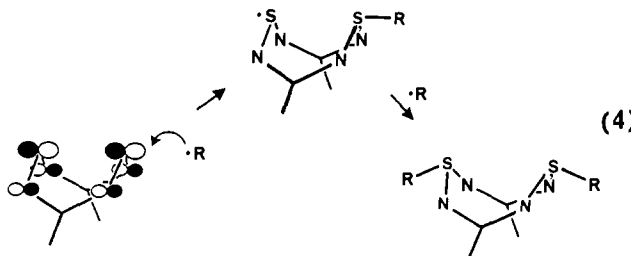
the case can be inferred from the absence of any \equiv S(O)ON(CF₃)₂ containing products, which would be formed (by competitive attack of ON(CF₃)₂) if \equiv SO-N(CF₃)₂ bond cleavage occurred to give separate N(CF₃)₂ and " \equiv SO" radicals.³⁵ The cis ligand sub-

Scheme III



stitution pattern observed for **2**, therefore, establishes an overall cis stereochemistry for the oxidation step itself.

The cis addition of the strongly nucleophilic radical ON(CF₃)₂ to **4** parallels the behavior of S₄N₄ and suggests that here too the transition state for the radical oxidation is controlled by the interaction of the radical SOMO with the low-lying LUMO of **4**. Accordingly the reaction can be envisaged in terms of the attack of a radical along a line parallel rather than perpendicular to the S-S vector (eq 4). Uptake of a second radical must then follow the stereochemistry of the first attack, affording an overall cis addition.



Summary and Conclusion

Regardless of whether or not there exists any substantial transannular S-S binding in folded dithiatetrazocines, the energies and distributions of their frontier orbitals can be used to predict both their kinetic susceptibility to oxidation via polar and free radical pathways and the stereochemistry of the products arising therefrom. Consistently (Me₂N)₂C₂N₄S₂ is less easily oxidized by radical oxidants than is S₄N₄, reacting only slowly with nucleophilic radicals such as ON(CF₃)₂, while with polar oxidants it reacts more rapidly. These reactivity patterns are more accentuated in diphosphadithiatetrazocines R₄P₂N₄S₂, which react rapidly with chlorine and bromine via polar pathways but appear not to react with any radical oxidants. In the case of the planar dithiatetrazocine Ph₂C₂N₄S₂ (**5**) oxidation cannot be effected by chlorine or (CF₃)₂NO; evidently the resistance of the π -system of this molecule to structural distortion is complemented by a thermodynamic resistance to chemical addition.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation (EPSCOR Grant ISP 8011447); and the State of Arkansas for financial support and for an NSERC post-doctoral fellowship (to R.T.B.). We thank Professor C. J. Willis for a generous gift of the CF₃NO used in this work and for obtaining the ¹⁹F NMR spectra.

Supplementary Material Available: Tables containing the hydrogen atom positions (S1, S2, S3) in [(Me₂N)₂C₂N₄S₂Cl]⁺[X]⁻ (X⁻ = Cl₃⁻ and PF₆⁻) and **2**, the phosphorus and fluorine coordinates in the PF₆⁻ salt (S2), and anisotropic thermal parameters (S4, S5, S6) (6 pages); observed and calculated structure factors for all three structures (39 pages). Ordering information is given on any current masthead page.

(30) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

(31) Burgi, H. B.; Dunitz, J. K. *Acc. Chem. Res.* **1983**, *16*, 153.

(32) Wang, C. S.-C.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 81.

(33) Emelêus, H. J.; Onak, T. *J. Chem. Soc. A* **1966**, 1291.

(34) Burton, C. A.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 5.

(35) Such pathways may be followed in the reactions of red phosphorus and SF₄ with ON(CF₃)₂ (ref 36 and 37), which do lead to E(O)ON(CF₃)₂ containing products. Consistently, the production of (CF₃)₂NON(CF₃)₂, presumably formed by the trapping of free N(CF₃)₂ with excess ON(CF₃)₂, is also observed.

(36) Spaziant, P. M. *MTP Internal. Rev. Sci.* **1972**, *3*, 141.

(37) Lott, J. A.; Babb, D. P.; Pullen, K. E.; Shreeve, J. M. *Inorg. Chem.* **1968**, *7*, 2593.