Formation and X-ray Structures of Eight- and Sixteen-Membered Rings $(ArC)_nN_{2n}(SPh)_n$ [$n = 2$, Ar = 4-XC_6H_4 (X = Br, CF_3); $n = 4$, Ar = 4-BrC_6H_4] and the Electronic Structures of $(HC)_2N_4(SH)_2$ and $(HC)_2N_4(SH)_2^{2-}$

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Optimum yields of heterocyclic products are obtained when the reaction of 4-$XC_6H_4CN_2(SiMe_3)_3$ (X = Br, CF_3) with PhSCl in a 1:3 molar ratio in CH_2Cl_2 is carried out at −100 °C followed by the mixture being warmed to −70 °C for 16 h. Under these conditions the eight-membered rings $(4\text{-}XC_6H_4)_2C_2N_4S_2Ph_2$ (**1b**, X = Br; **1c**, X = CF_3) are obtained in 64 and 80% yields, respectively, in addition to the purple diazenes *Z*,*E*,*Z*-PhSN(4-XC_6H_4)-CN=NC(C_6H_4X-4)NSPh (**2b**, 8%; **2c**, 19%) and, in the case of X = Br, the sixteen-membered ring $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$ (**3**) (8%). With a reaction time of 40 h the yield of **3** is increased to 25%. By contrast, the reaction of 3-$BrC_6H_4CN_2(SiMe_3)_3$ with 3 equiv of PhSCl at −70 °C gives *Z*,*E*,*Z*-PhSN(3-BrC_6H_4)CN=NC-(3-BrC_6H_4)NSPh in 75% yield. A possible pathway for the formation of cyclic products is proposed. The solid-state structures of **1b**, **1c**, and **3** were determined by X-ray crystallography. The eight-membered rings **1b** and **1c** adopt long boat conformations with the phenyl groups (attached to S) in equatorial positions. Density functional theory (DFT) calculations for the model ring system $(HC)_2N_4(SH)_2$ reveal that the observed C_{2v} geometry is the result of a second-order Jahn−Teller distortion of the planar (D_{2h}) structure. The chair conformer (C_{2h}) is only *ca*. 10 kJ mol^{-1} higher in energy than the boat conformer. The hypothetical dianion $(HC)_2N_4(SH)_2^{2-}$ is predicted to have a transannular S···S contact of about 2.5 Å. The sixteen-membered ring **3** has a cradle-like structure with S_4 symmetry.

Introduction

Since the seminal discovery of $C_2N_4S_2$ rings (dithiatetrazocines) in 1981,[1] heterocycles based on CNS frameworks have been the subject of numerous investigations.[2] Most of these studies have involved ring systems containing *two-coordinate* sulfur atoms, some of which form stable radicals that are of interest in the construction of molecular conductors.[2a,b] However, the original goal of generating hybrid CN/SN polymers from these ring systems has not been achieved.[3]

Carbon−nitrogen−sulfur heterocycles containing *three-* or *four*-coordinate sulfur atoms are also potential precursors of hybrid CN/SN polymers via ring-opening reactions. Although a wide variety of six-membered CNS(IV) ring systems is readily accessible,[4−8] much less is known about larger rings. The S,S′-dichloro derivative **1a** may be obtained by oxidative addition of Cl_2 across the S−S bond of the folded ring $(Me_2NC)_2N_4S_2$.[7a] Sulfur(II)-containing diazenes of the type **2** (R = Ar, R′ = Ph) are the thermodynamically stable products of the reactions of $ArCN_2(SiMe_3)_3$ with benzenesulfenyl chloride in a 1:3 molar ratio.[9,10] Preliminary evidence indicates that eight-membered rings of the type **1** are attainable under certain conditions.[9b] In the specific case where Ar = 4-$CF_3C_6H_4$, the eight-membered ring **1c** was obtained in addition to the isomeric diazene **2c**. However, the size of the heterocyclic ring **1c** was deduced from MS data alone, and X-ray structural information was lacking.

The initial objective of the present investigation was to optimize the yields of heterocycles by varying the conditions of the reaction of trisilylated benzamidines $ArCN_2(SiMe_3)_3$ with PhSCl, particularly with respect to the possible formation of larger ring systems. The influence of the position of the substituent attached to the C-aryl group on the nature of the products was also investigated. We describe here the synthesis and X-ray structures of the eight-membered rings, **1b** and **1c**, and the novel sixteen-membered ring **3**.[11] The eight-membered rings **1b** and **1c** were found to undergo photochemical isomer-

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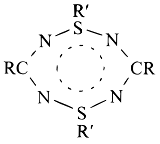
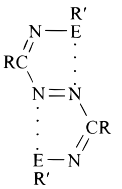
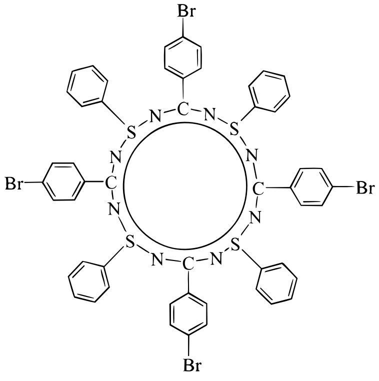


1a (R = NMe$_2$, R′ = Cl)
1b (R = 4-BrC$_6$H$_4$, R′ = Ph)
1c (R = 4-CF$_3$C$_6$H$_4$, R′ = Ph)



2a (E = S; R = R′ = 4-CH$_3$C$_6$H$_4$)
2b (E = S; R = 4-BrC$_6$H$_4$, R′ = Ph)
2c (E = S; R = 4-CF$_3$C$_6$H$_4$, R′ = Ph)
2d (E = S; R = 3-BrC$_6$H$_4$, R′ = Ph)



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ization to the corresponding diazenes **2b** and **2c**.[12] Density functional theory (DFT) calculations were carried out on the model system (HC)$_2$N$_4$(SH)$_2$ in order to explain the structural features of the C$_2$N$_4$S$_2$ ring and to provide a MO description of the photochemical process.

Experimental Section

All reactions, and the manipulation of reagents and products, were carried out under an atmosphere of dry nitrogen gas. The separation of products on silica gel columns or by TLC was performed under a solvent-rich atmosphere, and exposure to air was minimized. The reagents 2-XC$_6$H$_4$CN (X = Br, CF$_3$), 3-BrC$_6$H$_4$CN, 4-XC$_6$H$_4$CN (X = Br, CF$_3$), Ph$_2$S$_2$, and Me$_3$SiCl (all from Aldrich) were used as received; SO$_2$Cl$_2$ was distilled before use. LiN(SiMe$_3$)$_2$ (Aldrich) was dissolved in hexane and converted to the adduct LiN(SiMe$_3$)$_2$·OEt$_2$ by the addition of 1.1 equiv of diethyl ether. All solvents were dried by standard procedures and freshly distilled before used. The following reagents were prepared by the literature methods: PhSCl[13] and ArCN$_2$(SiMe$_3$)$_3$ (Ar = 3-BrC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$).[14]

Instrumentation. All ^{1}H NMR spectra were recorded on a Bruker ACE 200 spectrometer. The references for the spectra were the residual protons of deuterated solvents. Chemical shifts are quoted relative to tetramethylsilane ($\delta = 0$ ppm). Ultraviolet spectra were obtained by using a Cary 219 spectrometer. Infrared spectra were obtained as Nujol mulls on KBr plates with a Mattson 4030 FT-IR spectrometer. Mass spectra were measured on a Kratos MS80RFA instrument. All chemical analyses were carried out by the Analytical Services division of the Department of Chemistry, University of Calgary.

Reaction of 4-BrC$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ with PhSCl. This reaction was carried out several times under different conditions, and only a typical procedure is described here. Details of the product distribution obtained under various reaction conditions can be found in the Results and Discussion section.

A solution of PhSCl (0.770 g, 5.40 mmol) in CH$_2$Cl$_2$ (30 mL) was added dropwise to a solution of 4-BrC$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ (0.744 g, 1.79 mmol) in CH$_2$Cl$_2$ (50 mL) at −100 °C. After the addition the mixture was kept at −30 °C for 16 h to give a dark purple solution. Solvent and Me$_3$SiCl were removed under vacuum, and the residue was extracted with pentane (4 × 20 mL) to give Ph$_2$S$_2$ (0.37 g, 1.70 mmol, 95%). The pentane-insoluble solid was separated into PhSN(4-BrC$_6$H$_4$)CN=NC(4-BrC$_6$H$_4$)NSPh (**2b**) (0.30 g, 0.49 mmol, 55%), (4-BrC$_6$H$_4$)$_2$C$_2$N$_4$S$_2$Ph$_2$ (**1b**) (0.22 g, 0.36 mmol, 40%), and (4-BrC$_6$H$_4$)$_4$C$_4$N$_8$S$_4$Ph$_4$ (**3**) (30 mg, 5%) by the following procedure. The mixture of **1b**, **2b**, and **3** was dissolved in a large amount of CH$_2$Cl$_2$, and the solution was layered with diethyl ether. After 16 h the precipitated **2b** was separated by filtration. The filtrate (as a CH$_2$Cl$_2$ solution) was placed on a silica gel column and eluted with hexanes to remove **2b** and then with CH$_2$Cl$_2$ to separate **1b** and **3**. The last two fractions were monitored by UV light over a TLC plate. All three fractions were reduced in volume by vacuum transfer and layered with diethyl ether to produce crystalline products. The diazene **2b** was obtained as violet needles. Mp: 193 °C dec. Anal. Calcd for C$_{26}$H$_{18}$Br$_2$N$_4$S$_2$: C, 51.16; H, 2.97; N, 9.18. Found: C, 49.95; H, 2.87; N, 9.07. ^{1}H NMR (in CDCl$_3$, δ): 8.30 (d, C$_6$$H_4$, 2), 7.72 (d, C$_6$$H_4$, 2), 7.75 (m), 7.52 (m) and 7.38 (m, C$_6$$H_5$, 5). UV−vis (in CH$_2Cl_2$): $\lambda_{\max}$ 543 nm, $\epsilon = 1.7 \times 10^4$ M^{-1} cm^{-1}. The eight-membered ring **1b** was obtained as yellow needles. Mp: 199 °C (decomposed to give a purple melt). Anal. Calcd for C$_{26}$H$_{18}$Br$_2$N$_4$S$_2$: C, 51.16; H, 2.97; N, 9.18. Found: C, 50.86; H, 2.60; N, 8.95. ^{1}H NMR (in CDCl$_3$, δ): 8.16 (m) and 7.68 (m, C$_6$$H_5$, 5H), 8.05 (d, C$_6$$H_4$, 2), 7.47 (d, C$_6$$H_4$, 2). The sixteen-membered ring **3** was obtained as colorless, rectangular prisms. Mp: 211 °C dec. Anal. Calcd for C$_{52}$H$_{36}$Br$_4$N$_8$S$_4$: C, 51.16; H, 2.97; N, 9.18. Found: C, 50.66; H, 2.71; N, 8.95. ^{1}H NMR (in CDCl$_3$, δ): 7.65−7.40 (m, C$_6$$H_5$ and d, C$_6$$H_4$, 7), 6.95 (d, C$_6$$H_4$, 2).

Reaction of 4-CF$_3$C$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ and PhSCl. A solution of PhSCl (1.30 g, 9.10 mmol) in CH$_2$Cl$_2$ (50 mL) was added dropwise to a solution of 4-CF$_3$C$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ (1.16 g, 2.87 mmol) in CH$_2$Cl$_2$ (80 mL) at −100 °C. The yellow solution was kept at −78 °C for 16 h and became purple. Solvent and Me$_3$SiCl were pumped off, and the solid residue was extracted with pentane (4 × 15 mL) to give Ph$_2$S$_2$ (0.60 g, 2.75 mmol, 96%). The pentane-insoluble solid was dissolved in CH$_2$Cl$_2$ and filtered to remove a purple solid identified as PhSNC(4-CF$_3$C$_6$H$_4$)N=NC(4-CF$_3$C$_6$H$_4$)NSPh (**2c**) (0.26 g, 0.44 mmol, 19%). Mp: 205 °C. Anal. Calcd for C$_{28}$H$_{18}$F$_6$N$_4$S$_2$: C, 57.14; H, 3.08; N, 9.52. Found: C, 56.23; H, 2.58; N, 9.14. UV−vis (in CH$_2$Cl$_2$): $\lambda_{\max}$ 541 nm, $\epsilon = 2.2 \times 10^4$ M^{-1} cm^{-1}. ^{1}H NMR (in CDCl$_3$, δ): 8.50 (d, C$_6$$H_4$, 2), 7.50 (d, C$_6$$H_4$, 2), 7.80 (m), 7.55 (m), and 7.38 (m, C$_6$$H_5$, 5). The filtrate contained mainly (4-CF$_3$C$_6$H$_4$)$_2$C$_2$N$_4$S$_2$Ph$_2$ (**1c**) (1.13 g, 1.92 mmol, 80%), which was purified by recrystallization from CH$_2$Cl$_2$/diethyl ether in a closed vessel to give yellow needles of **1c**·0.5CH$_2$Cl$_2$. When crystallization was achieved by the slow evaporation of solvent, some colorless crystals of the unsolvated product were obtained and mixed with the yellow needles. Both types of crystals were analyzed by X-ray diffraction (see Results and Discussion). An analytical sample was obtained by subjecting the powdered yellow crystals to a dynamic vacuum for 3 days to remove solvent of crystallization. Mp: 178 °C (decomposed to a purple melt). Anal. Calcd for C$_{28}$H$_{18}$F$_6$N$_4$S$_2$: C, 57.14; H, 3.08; N, 9.52. Found: C, 57.56; H, 2.15; N, 9.23. ^{1}H NMR (in CDCl$_3$, δ): 8.30 (d, C$_6$$H_4$, 2), 7.62 (d, C$_6$$H_4$, 2), 8.20 (m) and 7.70 (m, C$_6$$H_5$, 5).

Reaction of 3-BrC$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ with PhSCl. A solution of PhSCl (1.71 g, 12.0 mmol) in CH$_2$Cl$_2$ (50 mL) was added dropwise to a solution of 3-BrC$_6$H$_4$CN$_2$(SiMe$_3$)$_3$ (1.85 g, 4.46 mmol) in CH$_2$Cl$_2$ (70 mL) at −100 °C. The mixture was kept at −78 °C for 16 h, during which time the yellow solution became purple. The solvent and Me$_3$SiCl were pumped off, and the solid residue was extracted with pentane (4 × 20 mL) to remove Ph$_2$S$_2$ (0.66 g, 3.03 mmol, 78%). The pentane-insoluble solid was dissolved in CH$_2$Cl$_2$. Addition of pentane to this solution and cooling to −30 °C gave purple crystals of PhSNC(3-BrC$_6$H$_4$)N=NC(3-BrC$_6$H$_4$)NSPh (**2e**) (0.88 g, 1.44 mmol, 75%). Mp: 200 °C. Anal. Calcd for C$_{26}$H$_{18}$Br$_2$N$_4$S$_2$: C, 51.16; H, 2.97; N, 9.18. Found: C, 51.00; H, 2.84; N, 9.08. UV−vis (in CH$_2$Cl$_2$): $\lambda_{\max}$ 544

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[11] A brief report on the X-ray structure of the sixteen-membered ring **3** appeared in the Proceedings of the Seventh International Symposium on Inorganic Ring Systems (IRIS VII) , Banff, Canada, August 1994. At that time the isolated yield of **3** was <1%. Zoricak, P.; Parvez, M.; Vargas-Baca, I.; Chivers, T. *Phosphorus, Sulfur Silicon Relat. Elem*. **1994**, *93−94*, 455.

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Table 1. Crystallographic Data for **1b**, **1c**, and **3**

	1b	**1c**	**1c**·$0.5CH_2Cl_2$	**3**
formula	$C_{26}H_{18}N_4S_2Br_2$	$C_{28}H_{18}N_4S_2F_6$	$C_{28}H_{18}N_4S_2F_6 \cdot 0.5CH_2Cl_2$	$C_{52}H_{36}N_8S_4Br_4$
fw	610.38	588.59	631.05	1220.77
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$I4_1/a$ (No. 88)
a, Å	25.383(9)	11.389(5)	27.417(6)	22.761(4)
b, Å	4.080(2)	13.472(4)	7.933(4)	
c, Å	23.181(3)	8.811(2)	26.772(7)	10.238(1)
α, deg		102.54(2)		
β, deg	95.31(2)	90.73(2)	111.07(3)	
γ, deg		84.25(3)		
V, Å^3	2390(1)	1312.9(7)	5433(3)	5303.9(7)
Z	4	2	8	4
T, °C	−103	23	−73	23
λ, Å	0.71069	0.71069	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.696	1.489	1.543	1.529
μ, cm^{-1}	36.00	2.72	3.63	32.45
R^a	0.045	0.049	0.055	0.038
$R_w{}^b$	0.043	0.045	0.055	0.020

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

nm, $\epsilon = 2.0 \times 10^4$ M^{-1} cm^{-1}. ^1H NMR (in $CDCl_3$, δ): 7.4−8.6 (m, C_6H_5 and 3-BrC_6H_4).

X-ray Analyses. All measurements were made on a Rigaku AFC6S diffractometer. Crystallographic data are summarized in Table 1.

1b. A yellow prismatic crystal (0.50 × 0.30 × 0.20 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained by a least-squares fit of the setting angles of 22 reflections in the range $18.57 < 2\theta < 24.19°$. Scans of $(1.68 + 0.34 \tan \theta)°$ were made at a speed of 8.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 2439 reflections were measured, of which 1051 had $I > 3.00\sigma(I)$. The data were corrected for Lorentz and absorption effects, and an empirical absorption correction was applied.[15] The structure was solved by direct methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Refinement converged with $R = 0.045$ and $R_w = 0.043$. For all four structures, scattering factors were those of Cromer and Waber,[18] and allowance was made for anomalous dispersion.[19] All calculations were performed using TEXSAN.[20]

1c. A colorless block (0.15 × 0.20 × 0.30 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained by a least-squares fit of the setting angles of 25 reflections in the range $18.81 < 2\theta < 23.68°$. Scans of $(1.26 + 0.34 \tan \theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 4635 reflections were measured, of which 1491 had $I > 3.00\sigma(I)$. The structure was refined by using SHELX76.[21a] The fluorine atoms of the CF_3 groups were disordered over two sites with unequal occupancy factors of 0.658(3), 0.342(3), 0.795(3), and 0.205(3) for F(1)−F(3), F(1*)−F(3*), F(4)−F(6), and F(4*)−F(6*), respectively. The F sites with the smaller occupancy factors were allowed isotropic temperature factors with the other F sites, and all non-hydrogen atoms were refined anisotropically. Refinement converged with $R = 0.048$ and $R_w = 0.045$.

1c·0.5CH₂Cl₂. A yellow prismatic crystal (0.45 × 0.30 × 0.15 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained by a least-squares fit of the setting angles of 22 reflections in the range $18.91 < 2\theta < 29.88°$. Scans of $(0.68 + 0.34 \tan \theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 5195 reflections were measured, of which 2128 had $I > 3.00\sigma(I)$. The procedures for data reduction, structure solution, and refinement were the same as those described for **1b**. A half molecule of CH_2Cl_2 per asymmetric unit was located in the lattice with one of the chlorine atoms disordered and lying on a 2-fold axis. Refinement converged with $R = 0.055$ and $R_w = 0.055$.

3. A colorless prismatic crystal (0.20 × 0.22 × 0.25 mm) was mounted on a glass fiber. Cell constants and an orientation matrix were obtained by a least-squares fit of the setting angles of 25 reflections in the range $20.00 < 2\theta < 35.80°$. Scans of $(1.10 + 0.34 \tan \theta)°$ were made at a speed of 4.0° min^{-1} to a maximum 2θ value of 50.1°. The intensities of 2504 reflections were measured, of which 717 had $I > 3.00\sigma(I)$. The procedures for data reduction, structure solution, and refinement were the same as those described for **1b**. Refinement converged with $R = 0.038$ and $R_w = 0.020$.

Computational Details

Details of the methods used for the DFT calculations have been described in a previous publication.[10]

Results and Discussion

Formation of Cyclic Products in the Reaction of $ArCN_2(SiMe_3)_3$ with PhSCl. The reaction of 4-$BrC_6H_4CN_2(SiMe_3)_3$ with PhSCl in a 1:3 molar ratio produces three products: the eight-membered ring $(4\text{-}BrC_6H_4)_2C_2N_4S_2Ph_2$ (**1b**), the *Z,E,Z* diazene PhSN(4-BrC_6H_4)CN═NC(4-BrC_6H_4)NSPh (**2b**), and the sixteen-membered ring $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$ (**3**) in addition to Ph_2S_2. Analysis of the reaction mixture by TLC (after removal of Ph_2S_2 by extraction with pentane) provides an easy identification of these three products which give rise to purple, pale yellow, and colorless bands for **2b**, **1b**, and **3**, respectively. The three products can be separated by chromatography on silica gel by using hexane as the eluent. For an efficient separation of the cyclic products **1b** and **3** it is necessary to remove as much of the purple diazene **2b** as possible prior to the chromatography step (see Experimental Section for details). The purity of each fraction can be readily determined by TLC or ^1H NMR spectra, since the resonances for the 4-BrC_6H_4 groups for **1b**, **2b**, and **3** appear as well-separated pseudodoublets of an AA′XX′ spin system, in different regions of the ^1H NMR spectrum.

The relative yields of the three products **1b**, **2b**, and **3** are markedly dependent on the reaction conditions, especially temperature, as indicated by the results of the experiments

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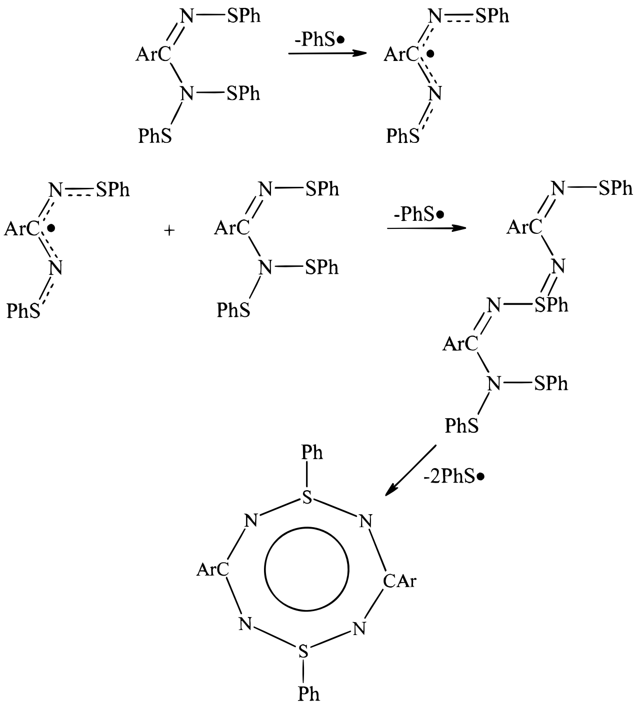
Table 2. Relative Yields (%) of Products from the Reaction of $4\text{-BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ with PhSCl (1:3 Molar Ratio)

reaction conditions		isolated yields (%)		
concn (M)[a]	temp (°C)[b]	**2b**	**1b**	**3**
0.24	−78 to 23	99		<1
0.016	−78 to 23	99	<1	
0.325	30	100		
0.287[c]	77	100		
0.036	−100 to −30	54.5	40	5.5
0.079	−100 to −78	8	64	8
0.034	−100 to −78[d]	17.5	37	25.5

[a] Concentration of $4\text{-BrC}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ in CH_2Cl_2. [b] The lower value indicates the temperature at which the addition of reagents occurred. Reactions were allowed to continue for *ca.* 16 h after reaching the higher temperature. [c] Solvent was CCl_4. [d] Reaction time was 40 h.

Scheme 1



summarized in Table 2. At room temperature (or above) the diazene **2b** is formed in essentially quantitative yields and the cyclic compounds **1b** and **3** are isolated in <1% yields. This observation is consistent with the results of DFT calculations which, for the model diazene HSN=C(H)N=NC(H)=NSH, predict that the *Z,E,Z* isomer **2** ($R = R' = H$) is the thermodynamically stable product, which is 155 kJ mol^{-1} lower in energy than the isomeric eight-membered ring.[10] However, substantial yields of the cyclic products **1b** and **3** can be obtained under kinetically controlled conditions. When the addition of reagents was carried out at −100 °C and the reaction mixture was maintained at −78 °C for 16 h, the yields of **1b** and **3** were 64 and 8%, respectively. The yield of the sixteen-membered ring **3** may be improved to 25% by allowing the reaction to continue at −70 °C for 40 h. An attempt was made to prepare another derivative of the novel sixteen-membered ring **3** by conducting the reaction of $4\text{-CF}_3\text{C}_6\text{H}_4\text{CN}_2(\text{SiMe}_3)_3$ with PhSCl under the conditions which were found to favor the formation of cyclic products. In this case, however, only two products were isolated. The purple diazene **2c** and the yellow eight-membered ring **1c** were obtained in yields of 19 and 80%, respectively. There was no evidence from TLC for the formation of a sixteen-membered ring.

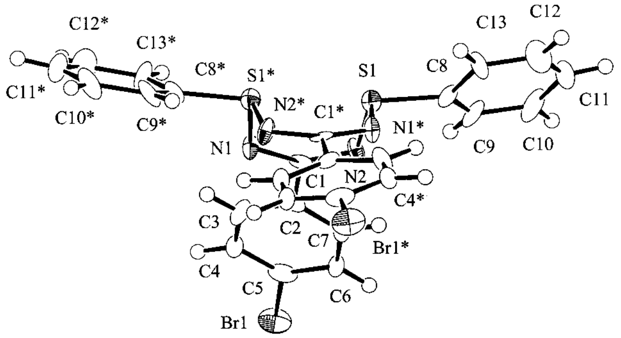


Figure 1. ORTEP drawing for $(4\text{-BrC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2\text{Ph}_2$, **1b**. Starred atoms are related by the symmetry operation $-x, y, {}^1/_2 - z$.

The synthesis of the cyclic products may be rationalized from the known mechanism of diazene formation.[22] The first stage involves replacement of the trimethylsilyl groups by thiophenolato groups to yield $\text{RCN}_2(\text{SPh})_3$. These species are thermally unstable and produce the resonance-stabilized radicals $\text{RC(NSPh)}_2^{\bullet}$. In a recent study we have shown that $\text{HC(NSPh)}_2^{\bullet}$ decays to the diazene PhSNC(H)N=NC(H)NSPh with a second-order rate law, which indicates that radical dimerization is the rate-determining step.[22] These radicals must be very reactive species, and as an alternative to dimerization, they could react with $\text{RCN}_2(\text{SPh})_3$ to form a longer-chain intermediate which, subsequently, cyclizes with loss of $\text{PhS}^{\bullet}$ to form eight-membered rings (Scheme 1). This ring formation pathway would have a first-order rate law with respect to radical concentration. Competition between the two processes can explain the observed trend in relative yields. At low temperature the decomposition of $\text{RCN}_2(\text{SPh})_3$ is slow so that only a small amount of $\text{RC(NSPh)}_2^{\bullet}$ is present and the first-order process will be dominant. At higher temperatures the concentration of $\text{RC(NSPh)}_2^{\bullet}$ increases. Consequently, the second-order pathway becomes faster, and the diazene is the main product.

The eight-membered rings **1b** and **1c** are pale yellow compounds that decompose at 199 and 178 °C, respectively, under ambient light to give purple melts which were shown to contain the corresponding diazenes **2b** and **2c**, respectively, by ^{1}H NMR spectroscopy. The sixteen-membered ring **3** is a colorless solid that decomposes at *ca.* 211 °C. The diazene **2b** is not one of the products of decomposition.

X-ray Structures of $(4\text{-XC}_6\text{H}_4)_2\text{C}_2\text{N}_4\text{S}_2\text{Ph}_2$ (1b, X = Br; 1c, X = CF_3). The X-ray structures of **1b** and **1c** were carried out in order to determine the conformation of the $\text{C}_2\text{N}_4\text{S}_2$ ring and, in particular, for comparison with the structures of related $\text{P}_2\text{N}_4\text{S}_2$ rings (in $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R}_2$) which are known to adopt either boat or chair conformations.[23] The initially formed boat conformers of $\text{Ph}_4\text{P}_2\text{N}_4\text{S}_2\text{R}_2$ are the kinetic products, which isomerize slowly in solution to the corresponding chair conformers.[24] ORTEP drawings of **1b** and **1c** with the atomic numbering schemes are displayed in Figures 1 and 2, respectively, and selected bond lengths and bond angles are compared in Table 3. Both $\text{C}_2\text{N}_4\text{S}_2$ rings adopt a boat conformation with sulfur atoms in the prow and stern positions, and the substituents attached to sulfur equatorially. The structure of **1c** was determined for a colorless crystal of the unsolvated compound and a yellow needle containing $0.5\text{CH}_2\text{Cl}_2$ of solvation (see Experimental Section). There are no significant differences in

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(22) Chivers, T.; McGarvey, B.; Parvez, M.; Vargas-Baca, I.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 3839.

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(24) Mean geometrical parameters for **1c** are calculated from the experimental data for **1c** and $\mathbf{1c}\cdot0.5\text{CH}_2\text{Cl}_2$.

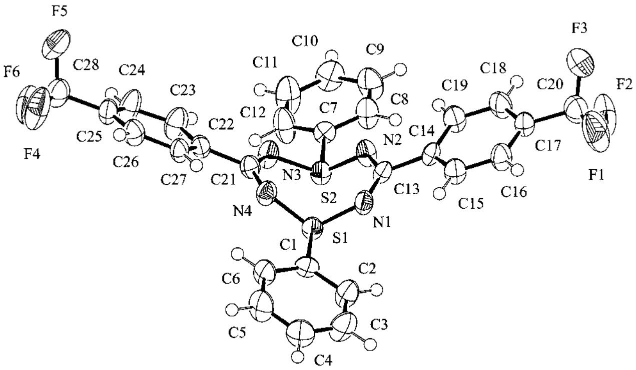


Figure 2. ORTEP drawing for $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2Ph_2$, **1c**.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $(4\text{-}XC_6H_4)_2C_2N_4S_2Ph_2$ (**1b**, X = Br; **1c**, X = CF_3)

Compound **1b**			
Bond Lengths			
S(1)−N(1)	1.661(7)	C(1)−N(2)	1.339(10)
S(1)−N(2)	1.650(7)	C(1)−C(2)	1.51(1)
C(1)−N(1)	1.328(9)	S(1)−C(8)	1.779(8)
Bond Angles			
N(1)*−S(1)−N(2)	110.8(4)	C(1)−N(1)−S(1)*	118.0(6)
N(1)*−S(1)−C(8)	98.4(4)	N(2)−C(1)−N(1)	135.1(7)
N(2)−S(1)−C(8)	99.2(4)	N(2)−C(1)−C(2)	112.1(7)
S(1)−N(2)−C(1)	118.6(6)	N(1)−C(1)−C(2)	112.7(7)
Compound **1c**·$0.5CH_2Cl_2$			
Bond Lengths			
S(1)−N(1)	1.651(6)	C(21)−N(3)	1.312(7)
S(1)−N(4)	1.634(6)	C(21)−N(4)	1.348(7)
S(2)−N(2)	1.623(5)	C(13)−C(14)	1.492(9)
S(2)−N(3)	1.652(5)	C(21)−C(22)	1.514(8)
C(13)−N(1)	1.319(7)	S(1)−C(1)	1.794(6)
C(13)−N(2)	1.330(7)	S(2)−C(7)	1.791(6)
Bond Angles			
N(1)−S(1)−N(4)	112.5(3)	S(2)−N(3)−C(21)	124.0(4)
N(1)−S(1)−C(1)	99.1(3)	C(21)−N(4)−S(1)	118.1(5)
N(4)−S(1)−C(1)	99.5(3)	N(1)−C(13)−N(2)	132.9(6)
N(2)−S(2)−N(3)	114.1(3)	N(1)−C(13)−C(14)	113.4(5)
N(2)−S(2)−C(7)	98.6(3)	N(2)−C(13)−C(14)	113.7(6)
N(3)−S(2)−C(7)	96.8(3)	N(3)−C(21)−N(4)	133.6(6)
S(1)−N(1)−C(13)	118.6(5)	N(3)−C(21)−C(22)	113.9(5)
C(13)−N(2)−S(2)	125.5(5)	N(4)−C(21)−C(22)	112.4(6)

the bond lengths and bond angles of the $C_2N_4S_2$ rings for these two crystals, but the packing in the unit cell differs considerably. Unsolvated **1c** contains two molecules in the unit cell whereas eight molecules of the heterocyclic ring and two CH_2Cl_2 molecules are accommodated within the unit cell of the solvated crystal.

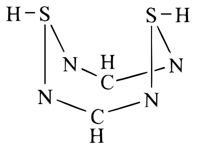
The mean S−N bond lengths are 1.655(7) and 1.644(6) Å, and the mean C−N distances are 1.333(10) and 1.321(7) Å for **1b** and **1c**,[24] respectively, indicating some π-delocalization within the rings. Consistently, the sums of the bond angles at the carbon atoms are 359.9° for **1b** and 360.0 and 359.9° for **1c**. The planar trigonal geometry is considerably distorted at the carbon atoms with endocyclic bond angles of 135.1(7)° for **1b** and a mean value of 133.9(6)° for **1c**. The endocyclic bond angles at S are 110.8(4)° for **1b** and 113.5(3)° for **1c** while the exocyclic ∠NSC bond angles are all less than 100°, reflecting the influence of nonbonding electrons on the sulfur atoms. The mean endocyclic bond angles at N are 118.3(6)° for **1b** and 121.4(5)° for **1c**. Each half of the eight-membered $C_2N_4S_2$ rings, represented by SNCNS units, is close to planar as indicated by the torsional angles of 7(1)° for S(1)*−N(1)−C(1)−N(2) and 11(1)° for S(1)−N(2)−C(1)−N(1) in **1b**. Interestingly, the S···S separations are 2.82, 2.95, and 2.94 Å for **1b**, **1c**, and **1c**·$0.5CH_2Cl_2$, respectively. These values are well within twice the van der Waals radius for S (3.7 Å).

Table 4. Calculated Molecular Dimensions for $(HC)_2N_4(SH)_2$ (**1d**) and the Dianion $(HC)_2N_4(SH)_2^{2-}$ (**1d**$^{2-}$)

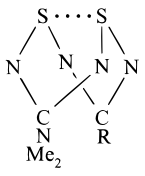
	1d(C_{2v})	**1d**(D_{2h})	**1d**(C_{2h})	exptl data[a]	**1d**$^{2-}$
Bond Distances (Å)					
C−N	1.327	1.320	1.331	1.329	1.341
N−S	1.710	1.757	1.705	1.645	1.877
S···S	3.260	3.249	3.247	2.88	2.537
Bond Angles (deg)					
N−C−N	139.4	139.6	135.2	133.9	134.4
C−N−S	122.6	122.9	118.6	120.5	113.8
N−S−N	124.9	154.6	130.1	112.5	156.3
R−S−N	92.9	102.7	92.8	98.8	85.2
Torsion Angles (deg)					
N−C−N−S	16.8	0	26.8	9.8	3.6
N−S−N−C	69.6	0	81.7	82.6	86.6

[a] The experimental data are average values taken from the X-ray structural determinations of **1b** and **1c**.

Theoretical Calculations: $(HC)_2N_4(SH)_2$ and $(HC)_2N_4(SH)_2^{2-}$. The synthesis, structures, and redox behavior of 1,5,2,4,6,8-dithiatetrazocine rings of the type $(RC)_2N_4S_2$ continue to attract attention.[24,25] In derivatives where R = aryl[1,25,26] the $C_2N_4S_2$ ring is a planar 10 π-electron system, whereas a folded structure **4** with d(S···S) = 2.4−2.5 Å is observed when one or both of the R groups is a dialkylamino group.[1,25a,27] Similar geometric distortions involving transannular S···S contacts are common in S−N heterocycles containing two-coordinate sulfur atoms, e.g., 1,5-$(Ph_3P)_2S_4N_4$[28] and 1,5-$R_4P_2N_4S_2$ (R = Me, Et, Ph).[29]



1d



4 (R = NMe_2 or Ph)

The observed C_{2v} structures for **1b** and **1c** resemble those of **4**. In this context, and in view of the unexpectedly short S···S separations of *ca.* 2.9 Å for **1b** and **1c**, it was of interest to determine the relative stabilities of the chair and boat conformers of the $C_2N_4S_2$ ring in the model system $(HC)_2N_4(SH)_2$ (**1d**). Approximate DFT theory has been applied successfully to modeling the properties of a variety of chalcogen−nitrogen compounds.[10,22,30] In this study the structure of **1d** was optimized on the basis of the C_{2v} structure determined for **1b** by X-ray crystallography. The calculated structure for **1d** is in reasonable agreement with the experimental data (see Table 4); the largest deviations are for parameters involving S atoms. The

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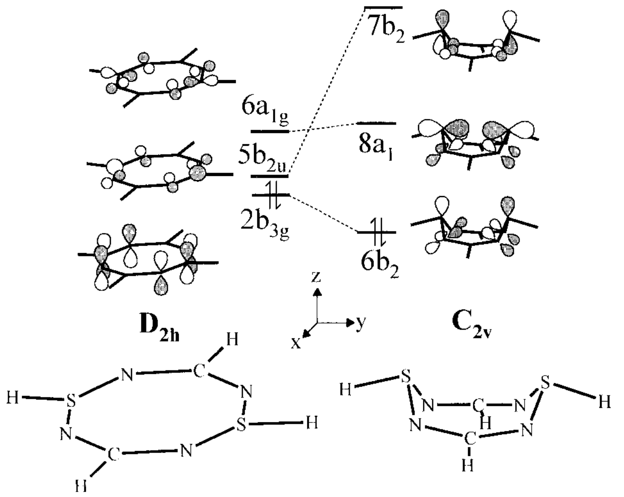

Figure 3. Qualitative correlation diagram for $(HC)_2N_4(SH)_2$ in D_{2h} and C_{2v} geometries.

observed C_{2v} geometry can be explained by considering a hypothetical planar (D_{2h}) structure. This optimized structure is a 12 π-electron system in which the HOMO($2b_{3g}$) lies just 0.12 eV below the LUMO($5b_{2u}$) (see Figure 3). It is predicted, therefore, that a second-order Jahn–Teller distortion will occur in the direction of the axis perpendicular to the molecular plane. In response to this effect the S atoms are lifted out of the plane. Consequently, the σ and π orbitals are mixed in the final MOs (see Figure 3). This change in geometry (from D_{2h} to C_{2v}) provides a stabilization energy of 267.8 kJ mol^{-1}. Indeed, the C_{2v} structure is the result of the same effect that leads to folding in **4** (R = NMe$_2$).[31] The relationship between **1d** and **4** (R = NMe$_2$) becomes apparent by considering that the attachment of two substituents to the S atoms brings about the occupation of the S–S antibonding orbital and, hence, the cleavage of the S···S interaction with the formation of a lone pair on each S atom. Although the calculations show that the most stable geometry for **1d** is C_{2v}, consistent with experimental observations, the chair conformer (C_{2h}) is only 9.5 kJ mol^{-1} higher in energy. The possible existence of conformational isomers of **1c** was investigated by ^{19}F NMR spectroscopy. However, only one isomer (presumably the boat conformer) was observed in CDCl$_3$ solution at 23 °C.

Despite the short S···S distance observed in **1b** and **1c**, no bonding interaction can be identified in the MOs of **1d**; however, consideration of the frontier orbitals of **1d** (see Figure 3) leads to an interesting prediction for the hypothetical dianion $(HC)_2N_4(SH)_2^{2-}$. The composition of the LUMO of **1d** is similar to that of the a_1 orbital which stabilizes the C_{2v} geometry of **4** (R = NMe$_2$).[31] This implies that $(HC)_2N_4(SH)_2^{2-}$ should also display a transannular S···S contact. The optimized structure of this dianion (see Table 4) does indeed predict a S···S interaction of about 2.5 Å. The NSN bond angles increase from *ca.* 125° in the neutral ring (C_{2v}) to *ca.* 156° in the dianion making the ring flatter. The predicted value of *ca.* 1.88 Å for *d*(S–N) implies very weak S–N bonds. We note, however, that (a) the predicted S–N distances for **1d** are *ca.* 0.06 Å longer than the experimental values (see Table 4) and (b) the S–N bond distances in the thermally stable compound $(C_6F_5S)_3N$ are greater than 1.8 Å.[32] Attempts to prepare the dianion of **1b** or **1c** will be the subject of a future investigation.

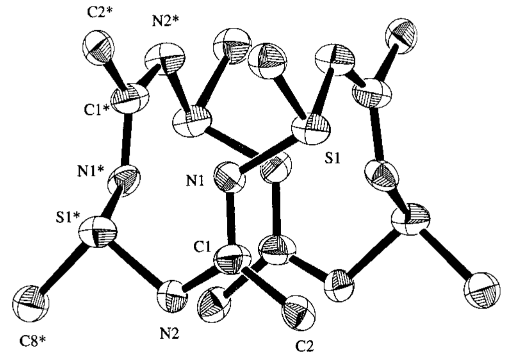

Figure 4. ORTEP drawing for $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$, **3**. For clarity only α-carbon atoms of aryl groups attached to the C and S atoms of the heterocyclic ring are shown. Starred atoms are related by the symmetry operation $^1/_4 - y + 1$, $^1/_4 + x - 1$, $^1/_4 - z$.

Photochemical Isomerization of 1b and 1c. Solid samples of **1b** or **1c** stored in a vial in daylight develop a purple taint after several weeks. The purple chromophore is readily attributed to the diazenes **2b** and **2c** on the basis of the characteristic visible absorption band at 540–545 nm. This identification was confirmed by ^{1}H NMR spectroscopy. The transformation of **1b** into **2b** occurs at a convenient rate under the influence of UV irradiation to allow the kinetics to be determined. A combination of kinetic data and DFT calculations, which were reported in a preliminary communication,[12] reveal that this is a first-order, i.e., intramolecular, process that is thermally symmetry forbidden, but photochemically allowed. The total reaction enthalpy for the isomerization of the model ring system **1d** into the corresponding diazene is −154.7 kJ mol^{-1}. The driving force is the formation of a very stable N=N bond at the expense of the elongation of two S–N bonds. Although molecular rearrangements are common for π-electron-rich S–N compounds,[31] there is only one previous report of a photochemical isomerization of a CNS heterocycle.[33] This involves the transformation of 1,3,2,4-dithiadiazoles into the 1,2,3,5 isomers, which occurs by a *bimolecular* process in solution[33] and in the solid state.[34]

X-ray Structure of $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$ (3). As indicated in Figure 4, the structure of **3** consists of a sixteen-membered ring with alternating CN and SN groups arranged to give a cradle-like structure with S_4 symmetry.[11] The only other example of a sixteen-membered CNS ring has the composition $C_8N_4S_4$ with alternating CC and SN groups and SN and CN bond lengths of 1.692 and 1.293 Å, respectively.[35] Bond lengths and bond angles for **3** are summarized in Table 5. The mean S–N bond length is 1.658(7) Å, and there are two distinct C–N bond lengths of 1.317(9) and 1.359(9) Å. In contrast to the eight-membered $C_2N_4S_2$ rings, the endocyclic bond angle at C(1) is typical for a three-coordinate carbon. Although the exocyclic NCC bond angles have markedly different values, 115.9(8) and 124.6(9)°, the geometry at the carbon atoms is perfectly planar ($\sum\angle C(1) = 360°$). The endocyclic bond angle at S is 108.7(4)°, and, like **1b** and **1c**, the exocyclic bond angle ∠SNC is <100°. Interestingly, the endocyclic bond angles at N(1) and N(2) differ significantly (119.4(6) *vs* 111.7(6)°), but the larger angle is associated with the longer C–N bond. The N(1)–C(1)–N(2)–S(1) units are almost planar with a dihedral angle

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(32) The quality of this X-ray structure is very poor ($R = 0.115$, $R_w = 0.125$) . The reported values for *d*(S–N) are 1.795(18) , 1.806(14) , and 2.067(18) Å. Biehl, A.; Boese, R.; Haas, A.; Klare, C.; Peach, M. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1263.

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Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for $(4\text{-}BrC_6H_4)_4C_4N_8S_4Ph_4$ (**3**)

Bond Lengths			
S(1)−N(1)	1.649(7)	C(1)−N(2)	1.317(9)
S(1)−N(2)	1.667(7)	S(1)−C(8)	1.785(9)
C(1)−N(1)	1.359(9)	C(1)−C(2)	1.49(1)
Bond Angles			
N(1)−S(1)−N(2)*	108.7(4)	C(1)−N(2)−S(1)*	111.7(6)
N(1)−S(1)−C(8)	99.3(4)	N(1)−C(1)−N(2)	119.5(8)
N(2)*−S(1)−C(8)	97.6(4)	N(1)−C(1)−C(2)	124.6(9)
S(1)−N(1)−C(1)	119.4(6)	N(2)−C(1)−C(2)	115.9(8)

of 3(1)° while the C(1)−N(1)−S(1)−N(2) units have a torsional angle of −78.8(8)°. The four N(1) nitrogen atoms form a square with edges of 3.07 Å so that there is sufficient room to accommodate a metal ion of radius 1.42 Å (e.g., K^+) in the central cavity of this macrocycle.

Influence of Aryl Substituents on the $ArCN_2(SiMe_3)_3$/3PhSCl Reaction. The position of the substituent attached to the C-aryl group has a dramatic influence on the nature of the products obtained from the $ArCN_2(SiMe_3)_3$/3PhSCl reaction. In a previous report[10] we have shown that $2\text{-}BrC_6H_4$ or $2\text{-}CF_3C_6H_4$ groups give rise to diazenes of the type PhSN═C(Ar)N═NC(Ar)═NSPh with an *E*,*E*,*E* rather than *Z*,*E*,*Z* geometry with respect to the N═C, N═N, and C═N double bonds. In the present work red products tentatively identified as the *E*,*E*,*E* isomers of **2b** and **2c** were evident in the TLCs of the $4\text{-}(XC_6H_4)CN_2SiMe_3$ (X = Br, CF_3)/3PhSCl reaction mixtures, but isomerization to the purple *Z*,*E*,*Z* diazenes occurred during the workup procedure. DFT calculations for model diazenes show that the *Z*,*E*,*Z* isomers of type **2** are the most thermodynamically stable.[10] It is apparent that, in addition to enforcing the *E*,*E*,*E* structure, the 2-Br (or $2\text{-}CF_3$) substituents also impede the thermal isomerization to the corresponding *Z*,*E*,*Z* isomers. In view of the remarkable effect of *ortho* substituents on the C-aryl group the reaction of $3\text{-}BrC_6H_4CN_2(SiMe_3)_3$ with 3 equiv of PhSCl under kinetically controlled conditions was also investigated. This reaction produces the purple diazene *Z*,*E*,*Z*-PhSN$(3\text{-}BrC_6H_4)$CN═NC$(3\text{-}BrC_6H_4)$NSPh (**2e**) in 75% yield, and no cyclic products were detected by TLC.

Conclusion. Eight-membered rings of the type $(4\text{-}XC_6H_4)_2\text{-}C_2N_4S_2Ph_2$ (X = Br, CF_3) can be obtained as boat conformers in good yields, and the sixteen-membered ring $(4\text{-}BrC_6H_4)_4\text{-}C_4N_8S_4Ph_4$ is formed in reasonable amounts when the reaction of $(4\text{-}XC_6H_4)CN_2(SiMe_3)_3$ with PhSCl (1:3 molar ratio) is carried out at very low temperatures (i.e., under kinetic control). Samples of the eight-membered $C_2N_4S_2$ rings should be stored in the dark to avoid photochemical decomposition to the corresponding diazenes. DFT calculations indicate that (a) boat and chair conformers of the $C_2N_4S_2$ ring have similar energies and (b) the dianions of heterocycles of the type **1** should exhibit transannular S···S interactions. The nature of the products obtained from the $ArCN_2(SiMe_3)_3$/3PhSCl is markedly dependent on the Ar group. When Ar = $2\text{-}XC_6H_4$ (X = Br, CF_3), the red *E*,*E*,*E* diazenes PhSN═C(Ar)N═NC(Ar)═NSPh are obtained, whereas for Ar = $3\text{-}BrC_6H_4$ only the *Z*,*E*,*Z* diazene was isolated.

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Supporting Information Available: Tables of experimental details for the crystal structure determinations, atomic coordinates, anisotropic thermal parameters, hydrogen atom coordinates and *U* values, bond lengths, bond angles, and torsion angles (34 pages). Ordering information is given on any current masthead page.

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