

129.0, 129.4, 131.9, 133.0, 137.3, 138.1, 138.2, 138.6, 138.9, 144.2, 145.0, 145.3, 147.8 (ring carbons). Exact mass calcd for $C_{45}H_{66}Si_4O$: 734.4189. Found: 734.4189.

Reaction of 11 with Methanol. A mixture of 14.3 mg (0.0204 mmol) of **11**, 0.2 mL of methanol, and 0.05 mL of dry cyclohexane was heated in a sealed tube at 120 °C for 1 h. The remaining methanol and cyclohexane was evaporated to give 14.9 mg (100%) of **15**. All spectral data for **15** were identical with those of an authentic sample.

Acknowledgment. We are indebted to the Crystallographic Research Center, Institute for Protein Research, Osaka University, for X-ray data collection and computer calculations. We also express our appreciation to Shin-etsu Chemical Co., Ltd., Toshiba

Silicone Co., Ltd., and Toray Silicone Co., Ltd. for a gift of organochlorosilanes.

Registry No. 1, 75529-55-4; **2**, 79184-72-8; **3**, 83846-03-1; **4**, 75535-87-4; **6**, 79184-71-7; **7**, 75529-54-3; **8**, 83846-02-0; **9**, 75529-57-6; **10**, 99053-93-7; **11**, 99053-94-8; **12**, 99053-95-9; **13**, 99053-96-0; **14**, 99053-97-1; **15**, 99053-98-2; $(\text{Mes})_2\text{SiCl}_2$, 5599-27-9; Me_3SiCl , 75-77-4; Me_3NO , 1184-78-7.

Supplementary Material Available: Tables of fractional coordinates, temperature factors, bond distances, and angles for **14** (6 pages). Ordering information is given on any current masthead page.

Preparation and Interconversion of Dithiatriazine Derivatives: Crystal, Molecular, and Electronic Structure of Bis(5-phenyl-1,3,2,4,6-dithiatriazine) $(\text{PhCN}_3\text{S}_2)_2$

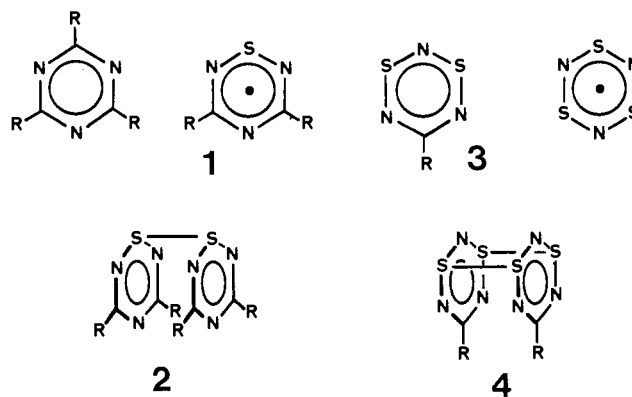
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Contribution from the Guelph Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. Received July 8, 1985

Abstract: The reaction of *N,N,N'*-tris(trimethylsilyl)benzamidine with $\text{S}_3\text{N}_3\text{Cl}_3$ yields PhCN_3S_3 , a bicyclic 5-phenyl-1,3,2,4,6-dithiatriazine derivative with an $-\text{NSN}-$ unit bridging the 1,3-sulfur atoms. Oxidation of this compound with chlorine produces 5-phenyl-1,3-dichloro-1,3,2,4,6-dithiatriazine ($\text{PhCN}_3\text{S}_2\text{Cl}_2$) which, upon reduction with triphenylstibine, affords the dimeric species bis(5-phenyl-1,3,2,4,6-dithiatriazine) $(\text{PhCN}_3\text{S}_2)_2$. The crystal and molecular structure of this dimer has been determined by single-crystal X-ray diffraction. The compound crystallizes in the space group $P\bar{1}$, $a = 6.093$ (2) Å, $b = 10.874$ (4) Å, $c = 12.458$ (5) Å, $\alpha = 109.13$ (3)°, $\beta = 100.59$ (3)°, $\gamma = 92.52$ (3)°, $V = 762$ (1) Å³, and $Z = 2$. The structure was solved by direct methods and refined by full-matrix least-squares and Fourier methods to give a final $R = 0.051$ for 1327 reflections with $I > 3\sigma(I)$. The dimer consists of a cofacial arrangement of two 5-phenyl-1,3,2,4,6-dithiatriazine units linked (formally) by two long (2.527 (3) Å) S---S interactions. The two planar SNCNS segments within each dimer are mutually inclined with a dihedral angle of 12.5°. Dimeric pairs are stacked in a head-to-tail fashion with a 3.65-Å interplanar separation between each phenyl ring and its neighboring CN_3S_2 ring. MNDO molecular orbital calculations on a model HCN_3S_2 system reveal a triplet ground state; the dimerization process is interpreted in terms of the association of the π -systems of two HCN_3S_2 units.

The discovery of the metallic² and superconducting³ properties of the $(\text{SN})_x$ polymer has stimulated research into the design of related polymeric and molecular systems that emulate its unique properties.⁴ This work has led to the development of a range of hybrid organothiazyl molecules and polymers which, in principle at least, combine the unusual electronic attributes of conjugated thiazyl linkages (high electron affinities, low ionization potentials) with the stabilizing influence of a carbon-based framework.⁵⁻¹³

Scheme I



Our own efforts in this area have resulted in the characterization of the remarkably stable 7π -electron thiatriazinyl radical **1** (R

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= Ph) which, in the solid state, exists as the cofacial dimer **2** (Scheme I).¹³ As a continuation of this work, we have pursued examples of the 8π -electron dithiatriazine ring system **3**, the isolation of which would complete the heterocyclic series $(CR)_nS_{3-n}N_3$ (Scheme I). The remaining inorganic member of this series, the 9π -electron S_3N_3 radical, has recently been identified as the gas-phase species produced from the vaporization of $(SN)_x$ polymer.¹⁴

Herein we describe an efficient and rational synthetic sequence to a range of dithiatriazine derivatives.¹⁵ Our attempts to prepare **3** (R = Ph) have led to the isolation of the unusual dimeric system **4**. This structure has been confirmed by a single-crystal X-ray analysis, which reveals a cofacial arrangement of the two dithiatriazine rings linked (formally) by two long interannular S-S interactions. In order to evaluate the electronic factors which dictate this association process, we have carried out a series of MNDO molecular orbital calculations on a model HCN_3S_2 monomer and a model $(HCN_3S_2)_2$ dimer. The results of this analysis are related to the structural properties of other thiazyl heterocycles and binary sulfur nitride derivatives.

Experimental Section

Starting Materials and General Procedures. *N,N,N'*-Tris(trimethylsilyl)benzamidine,¹⁶ *N,N'*-bis(trimethylsilyl)sulfur diimide,¹⁷ and $S_3N_3Cl_3$ ¹⁸ were prepared according to literature methods. Chlorine gas (Matheson), triphenylstibine, and norbornadiene (Aldrich) were obtained commercially and were used as received. The solvents carbon tetrachloride, chloroform, and methylene chloride were dried before use by distillation from P_2O_5 . Acetonitrile was double-distilled from P_2O_5 and calcium hydride. All reactions were carried out under an atmosphere of nitrogen gas. Infrared spectra were recorded on a Perkin-Elmer 1330 grating spectrophotometer. ¹H NMR spectra were recorded at 400 HMZ on a Bruker WH-400 spectrometer. Individual proton assignments on **7** were made on the basis of a two-dimensional COSY experiment; these correct the tentative assignments of our earlier communication.¹⁵ Low-resolution electron impact mass spectra were recorded on a VG 7070 EF spectrometer at 70 eV, samples being admitted through conventional inlet systems. Elemental analyses were performed by MHW laboratories, Phoenix, AZ.

Preparation of $PhCN_3S_3$ (5**).** A solution of $PhCN(SiMe_3)_2NSiMe_3$ (14.0 g 41.6 mmol) in 70 mL of acetonitrile was added over a 5-min period to a stirred solution of $S_3N_3Cl_3$ (10.0 g, 40.9 mmol) in 200 mL of acetonitrile. During the addition the reaction vessel was cooled by an ice/water bath. The flocculent yellow crystalline precipitate that was produced was filtered under nitrogen, washed with two 10-mL aliquots of acetonitrile, and dried in vacuo. The crude product $PhCN_3S_3$ (**5**) (8.22 g, 32.2 mmol, 79%) was recrystallized from hot acetonitrile as yellow-orange air-stable plates, 136 °C dec. Anal. Calcd for $C_7H_5N_3S_3$: C, 32.93; H, 1.97; N, 27.43%. Found: C, 32.89; H, 2.46; N, 27.93%. Mass spectrum, m/z 195 ($PhCN_3S_2^+$, 23%), 181 ($PhCN_2S_2^+$, 75%), 149 ($PhCN_2S^+$, 29%), 135 ($PhCNS^+$, 30%), 103 ($PhCN^+$, 100%); IR (1600–250-cm⁻¹ region) 1595 (w), 1400 (w), 1365 (s, br), 1335 (s, br), 1290 (m), 1170 (s), 1150 (s), 1070 (s), 1000 (vs), 930 (m), 925 (m), 855 (w), 815 (m), 790 (sh), 775 (vs), 750 (sh), 720 (s), 700 (vs), 685 (sh), 670 (s), 650 (sh), 575 (s), 500 (s), 465 (m), 400 (w), 370 (w), 345 (w), 295 (w); ¹³C NMR δ (endocyclic carbon) 165.8.

Preparation of $PhCN_3S_2Cl_2$ (6**).** Chlorine gas was passed over a slurry of $PhCN_3S_3$ (**5**) (6.00 g, 23.5 mmol) in 150 mL of carbon tetrachloride for approximately 5 min and the resulting suspension allowed to react for an additional 30 min. The mixture was then filtered under nitrogen (to remove a small quantity of $PhCN_2S_2Cl^{19}$) and the filtrate reduced to dryness in vacuo. The residual solid was recrystallized from a methylene chloride/hexane as yellow moisture-sensitive plates of $PhCN_3S_2Cl_2$ (**6**) (4.62 g, 17.4 mmol, 74%), mp 119–121 °C. Anal. Calcd for $C_7H_5N_3S_2Cl_2$: C, 31.59; H, 1.89; N, 15.79; Cl, 26.64%. Found: C, 31.80; H, 2.07; N, 15.67; Cl, 26.51%. Mass spectrum, m/z 230 ($PhCN_3S_2Cl^+$, 2%), 195 ($PhCN_3S_2^+$, 39%), 181 ($PhCN_2S_2^+$, 11%), 149 ($PhCN_2S^+$, 46%), 135 ($PhCNS^+$, 13%), 103 ($PhCN^+$, 50%), 46 (NS^+ , 100%); IR (1600–250-cm⁻¹ region) 1595 (w), 1365 (sh), 1340 (s, br), 1190 (sh), 1180 (m, br), 1090 (w), 1065 (w), 1025 (m), 910 (s), 790 (s), 700 (s), 660 (w), 530 (w), 495 (m), 420 (m), 375 (m), 310 (m).

Reaction of $PhCN_3S_2Cl_2$ (6**) with $Me_3SiNSNSiMe_3$.** A solution of $Me_3SiNSNSiMe_3$ (0.31 g, 1.50 mmol) in 1.5 mL of CH_2Cl_2 was added to a stirred slurry of $PhCN_3S_2Cl_2$ (**6**) (0.40 g, 1.50 mmol) in 4 mL of CH_2Cl_2 . After 45 min, the yellow solid was collected by filtration and recrystallized from hot acetonitrile to give golden plates of $PhCN_3S_3$ (**5**) (0.30 g, 1.18 mmol, 78%), the authenticity of which was confirmed from its melting point and infrared spectrum.

Preparation of $(PhCN_3S_2)_2$ (4**).** A solution of triphenylstibine (0.66 g, 1.87 mmol) in 20 mL of $CHCl_3$ was added dropwise to a stirred solution of $PhCN_3S_2Cl_2$ (**6**) (0.50 g, 1.87 mmol) in 30 mL of $CHCl_3$. A buff-colored microcrystalline precipitate of $(PhCN_3S_2)_2$ (**4**) (0.28 g, 0.15 mmol, 78%), mp 115 °C, was immediately produced. This material was analytically pure. Anal. Calcd for $C_{14}H_{10}N_6S_4$: C, 43.06; H, 2.58; N, 21.52; S, 32.84%. Found: C, 43.34; H, 2.80; N, 21.79; S, 32.61%. Mass spectrum, m/z 195 ($PhCN_3S_2^+$, 19%), 181 ($PhCN_2S_2^+$, 6%), 149 ($PhCN_2S^+$, 21%), 135 ($PhCNS^+$, 3%), 103 ($PhCN^+$, 25%), 92 ($S_2N_2^+$, 12%), 78 (S_2N^+ , 11%), 76 (?), 12%), 64 (S_2^+ , 9%), 46 (SN^+ , 100%). IR (1600–250-cm⁻¹ region) 1590 (w), 1450 (s), 1390 (m), 1330 (s, br), 1180 (sh), 1170 (s), 1155 (s), 1090 (w), 1070 (w), 1060 (m), 1020 (m), 930 (m), 915 (m), 890 (vs), 850 (w), 805 (m), 780 (s), 765 (vs), 715 (w), 690 (m), 675 (vs), 665 (sh), 650 (w), 480 (m), 445 (s), 360 (s).

Reaction of $(PhCN_3S_2)_2$ (4**) with Chlorine.** Chlorine gas was bubbled slowly through a suspension of **4** (0.37 g, 0.95 mmol) in 15 mL of CCl_4 . After 3 h, the mixture was filtered and the solvent removed in vacuo from the filtrate to leave **6** (0.43 g, 1.62 mmol, 85%) as a microcrystalline yellow solid, identified by its infrared spectrum.

Preparation of $PhCN_3S_2C_7H_8$ (7**).** An excess of norbornadiene (~5 mL) was added to a slurry of $(PhCN_3S_2)_2$ (**4**) (0.45 g, 1.15 mmol) in 4 mL of acetonitrile and the resulting mixture stirred for 16 h. The resulting precipitate (0.42 g, 1.46 mmol, 63%) was recrystallized from hot acetonitrile to give colorless plates of $PhCN_3S_2C_7H_8$ (**7**), mp 179–180 °C. Anal. Calcd for $C_{14}H_{15}N_3S_2$: C, 58.71; H, 4.56; N, 14.62%. Found: C, 58.73; H, 4.47; N, 14.74%. Mass spectrum, m/z 287 ($PhCN_3S_2C_7H_8^+$, 1%), 259 ($PhCNS_2C_7H_8^+$, 2%), 195 ($PhCN_3S_2^+$, 100%), 149 ($PhCN_2S^+$, 41%), 103 ($PhCN^+$, 21%), 91 ($C_7H_7^+$, 19%); ¹H NMR ($CDCl_3$) δ 7.3–7.9 (m, 5 H, phenyl), 6.24 (s, 2 H, $H_{5,6}$), 4.48 (d, 2 H, $H_{2,3}$, $J = 1.5$ Hz), 3.24 (t, 2 H, $H_{1,4}$, $J = 1.7$ Hz), 2.08 and 1.16 (d, 1 H, H_7 and H_8 , $J_{7,8} = 9.8$ Hz); IR (1600–250-cm⁻¹ region) 1450 (s), 1380 (s), 1315 (vs), 1295 (m), 1285 (m), 1250 (m), 1210 (w), 1165 (m), 1150 (w), 1125 (m), 1060 (w), 1020 (w), 1000 (w), 970 (w), 930 (w), 905 (w), 860 (w), 820 (w), 790 (s), 775 (s), 760 (m), 745 (s), 730 (m), 705 (vs), 645 (m), 550 (w), 525 (m), 460 (w), 450 (w), 400 (w), 355 (w); ¹³C NMR δ (endocyclic carbon) 159.8.

X-ray Measurements. Crystals of $(PhCN_3S_2)_2$ (**4**) suitable for X-ray diffraction were obtained by recrystallization from chloroform. X-ray data were collected at ambient temperature by using an ENRAF Nonius CAD-4 diffractometer employing graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. The crystals grow as small, extremely thin platelets. Data sets were collected for two crystals; the one used for the data of this report measured $0.02 \times 0.14 \times 0.34$ mm and had $D_{\text{calcd}} = 1.71$ g cm⁻³ for $Z = 2$. The triclinic $P\bar{1}$ cell dimensions of $a = 6.093$ (2) Å, $b = 10.874$ (4) Å, $c = 12.458$ (5) Å, $\alpha = 109.13$ (3)°, $\beta = 100.59$ (3)°, $\gamma = 92.52$ (3)° and $V = 762$ (1) Å³ for $C_{14}H_{10}N_6S_4$ were determined by a least-squares analysis of the setting angles of 25 reflections. Variable scan rates with a $2\theta_{\text{max}}$ of 40° resulted in 2819 reflections measured for $h = -7$ to 7, $k = -12$ to 12, and $l = 0$ to 14; of these 1327 with $I > 3\sigma(I)$ were used for the structure solution and refinement. Reflections were corrected for absorption (transmission coefficients ranged from 0.93 to 1.00 for $\mu = 6.09$ cm⁻¹), and a 2.8% decay was indicated by the three reflections monitored during data collection.

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Table I. Fractional Atomic Coordinates, Isotropic Thermal Parameters, and Their ESD's

$B_{eq} = \langle f_j^2 \rangle (a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + ac B_{13} \cos \beta)$				
	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)/B$
S(1)	0.0313 (3)	0.8722 (2)	0.0314 (1)	2.69 (4)
S(2)	0.4469 (3)	0.7889 (2)	0.0073 (1)	2.82 (4)
S(3)	0.2085 (3)	1.0563 (2)	0.2170 (2)	2.74 (4)
S(4)	0.6253 (3)	0.9733 (2)	0.1934 (2)	2.95 (4)
N(1)	0.0119 (9)	0.7627 (5)	0.0890 (4)	2.4 (1)
N(2)	0.3740 (9)	0.6896 (5)	0.0682 (5)	2.8 (1)
N(3)	0.2179 (9)	0.9735 (5)	0.3008 (5)	2.7 (1)
N(4)	0.5775 (8)	0.8981 (5)	0.2792 (4)	2.5 (1)
N(5)	0.2454 (9)	0.8694 (5)	-0.0295 (4)	2.7 (1)
N(6)	0.4458 (9)	1.0748 (5)	0.1775 (5)	3.0 (1)
C(1)	0.175 (1)	0.6868 (6)	0.1010 (5)	2.2 (1)
C(2)	0.130 (1)	0.5871 (6)	0.1527 (5)	2.4 (1)
C(3)	-0.060 (1)	0.5850 (6)	0.1988 (6)	3.2 (2)
C(4)	-0.098 (1)	0.4919 (7)	0.2487 (7)	4.0 (2)
C(5)	0.049 (1)	0.4023 (6)	0.2547 (6)	3.4 (2)
C(6)	0.238 (1)	0.4030 (7)	0.2081 (6)	3.4 (2)
C(7)	0.277 (1)	0.4935 (6)	0.1571 (6)	2.9 (2)
C(8)	0.388 (1)	0.9051 (6)	0.3208 (5)	2.5 (1)
C(9)	0.373 (1)	0.8342 (6)	0.4020 (5)	2.6 (2)
C(10)	0.191 (1)	0.8427 (7)	0.4564 (6)	3.6 (2)
C(11)	0.172 (1)	0.7751 (8)	0.5306 (6)	4.4 (2)
C(12)	0.333 (1)	0.6980 (8)	0.5515 (6)	4.5 (2)
C(13)	0.515 (1)	0.6876 (8)	0.4989 (7)	4.5 (2)
C(14)	0.534 (1)	0.7551 (7)	0.4241 (6)	3.6 (2)

The structure was solved by direct methods (MULTAN11/82)²⁰ and refined by full-matrix least-squares analysis based on $(|F_o| - |F_c|)^2$. Hydrogen atoms were refined with isotropic thermal parameters and the non-hydrogen atoms were refined anisotropically for a total of 257 variables. The final R , R_w ,²¹ and GOF²² were 0.051, 0.059, and 1.40, respectively. The final difference map had a maximum of 0.53 e Å⁻³ and a minimum of -0.54 e Å⁻³, and the largest shift on the last refinement cycle was 0.01 Δ/σ. The weighting scheme was based on counting statistics with $p = 0.05$ and gave no systematic variation in $F/\sigma(F)$ as a function of F or $\sin \theta$. No secondary extinction corrections were made. Neutral atom scattering factors²³ were corrected for real and anomalous dispersion.²⁴ The computer programs used were those provided by the ENRAF Nonius structure determination package. Non-hydrogen atom coordinates are given in Table I, and selected bond distance and angle data are provided in Table II. Tables containing atom coordinates for the hydrogen atoms, anisotropic thermal parameters of non-hydrogen atoms, and structure factor amplitudes are available as supplementary material.

Theoretical Method and Models. The MNDO (modified neglect of diatomic overlap) method^{25a} has been used extensively for the study of the electronic structures of sulfur nitride derivatives. In the present work, calculations were performed on model RCN₃S₂ compounds using both the singlet and triplet (UHF half-electron method) options of the MOPAC^{25b} program. Reported heats of formation refer to single determinantal calculations. A singlet calculation performed on HCN₃S₂ with configuration interaction including the first two doubly excited configurations produced a lowering in energy (relative to the triplet) of less than 2 kcal/mol. We therefore conclude that, as observed elsewhere,²⁶ the inclusion of configuration interaction will not alter significantly the MNDO singlet/triplet energy differences. Full geometry optimization within the confines of C_{2v} symmetry was invoked in each case. Calculations on a model (HCN₃S₂)₂ dimer were carried out by using a pair of coplanar HC₂N₃S₂ units, the distance between which was allowed to

(20) Main, P. MULTAN11/82, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, University of York, England.

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

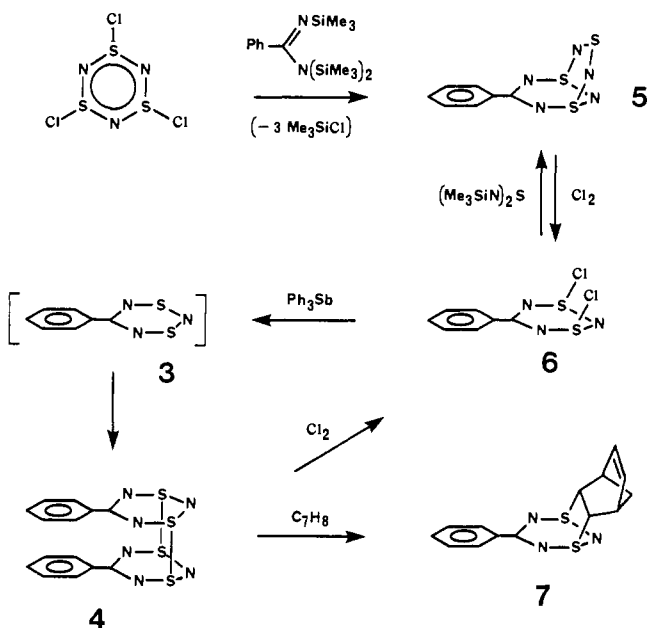
(22) GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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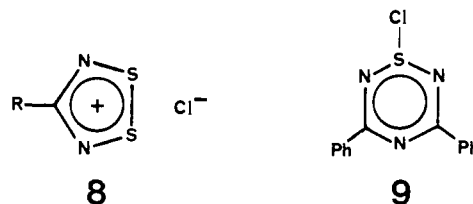
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Scheme II

optimize. Bond orders and charge densities refer to the elements of the Coulson density matrix.

Results and Discussion

Preparation of (PhCN₃S₂)₂ (4). Several derivatives based on the dithiatriazine framework have been prepared. The reaction of *N,N'*-dimethylguanidinium hydrochloride with S₃N₃Cl₂ produces 5-(dimethylamino)-1,3-dichloro-1,3,2,4,6-dithiatriazine in low yield,²⁷ while the corresponding 5-trifluoromethyl derivative can be isolated from the reaction of trifluoroacetonitrile with S₃N₃Cl₃.²⁸ This latter route has also been used to prepare the 5-NMe₂ compound.²⁹ However, neither method is generally applicable to the generation of 1,3-dichloro-1,3,2,4,6-dithiatriazines; for example, the reactions of benzamidinium hydrochloride and trichloroacetonitrile with S₃N₃Cl₃ yield the corresponding dithiadiazolium chloride **8** (R = Ph and CCl₃) rather than a dithiatriazine.^{19,30} To further complicate the issue, the reaction of benzamidine rather than its hydrochloride with S₃N₃Cl₃ yields the 1-chloro-1,2,4,6-thiatriazine **9**.¹³



We have therefore sought a more reliable and rational synthetic sequence to the dithiatriazine system and have discovered that the action of *N,N,N'*-tris(trimethylsilyl)benzamidinium on S₃N₃Cl₃ (see Scheme II) provides a direct high yield (~80%) route to the bicyclic molecule **5**, the structure of which consists of a 5-phenyl-substituted dithiatriazine with an -NSN- bridge straddling the 1,3-sulfur atoms. The reaction appears to offer a general route to both 5-alkyl and 5-aryl derivatives.³¹ The -NSN- bridge in **5** is readily cleaved by oxidation with chlorine to yield the desired 1,3-dichloro derivative **6**. Small amounts of the dithiadiazolium chloride **8** (R = Ph)¹⁹ and 1-chloro-thiatriazine **9**¹³ are also formed,

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(28) Höfs, H.-U.; Hartmann, G.; Mews, R.; Sheldrick, G. M. *Z. Naturforsch., B* **1984**, *39*, 1389.

(29) Chivers, T.; Richardson, J. F.; Smith, N. R. M. Paper presented at the 68th Canadian Chemistry Conference, Kingston, June, 1985, Abstract IN-B2-1.

(30) Höfs, H.-U.; Mews, R.; Clegg, W.; Noltemeyer, M.; Schmidt, M.; Sheldrick, G. M. *Chem. Ber.* **1983**, *116*, 416.

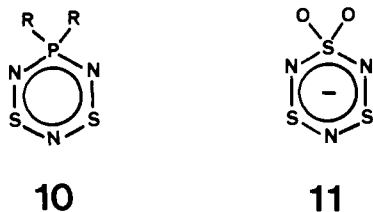
(31) Boerë, R. T.; Oakley, R. T., unpublished results.

Table II. Selected Bond Distances (Å), Bond Angles (deg) and Their ESD's

atom 1	atom 2	distance	atom 1	atom 2	atom 3	angle
S(1)	S(3)	2.526 (3)	N(1)	S(1)	N(5)	114.6 (3)
S(2)	S(4)	2.532 (3)	N(2)	S(2)	N(5)	113.5 (3)
S(1)	N(1)	1.590 (5)	N(3)	S(3)	N(6)	113.8 (3)
S(2)	N(2)	1.599 (5)	N(4)	S(4)	N(6)	114.1 (3)
S(3)	N(3)	1.581 (5)	S(2)	S(1)	S(3)	90.78 (8)
S(4)	N(4)	1.600 (5)	S(1)	S(2)	S(4)	89.33 (8)
S(1)	N(5)	1.622 (5)	S(1)	N(5)	S(2)	116.6 (3)
S(2)	N(5)	1.624 (5)	S(3)	N(6)	S(4)	116.3 (3)
S(3)	N(6)	1.635 (5)	S(1)	N(1)	C(1)	122.5 (4)
S(4)	N(6)	1.620 (6)	S(2)	N(2)	C(1)	123.0 (4)
N(1)	C(1)	1.339 (7)	S(3)	N(3)	C(8)	123.3 (5)
N(2)	C(1)	1.350 (7)	S(4)	N(4)	C(8)	122.4 (5)
N(3)	C(8)	1.334 (8)	N(1)	C(1)	N(2)	127.2 (5)
N(4)	C(8)	1.347 (7)	N(3)	C(8)	N(4)	127.4 (6)
C(1)	C(2)	1.471 (2)	N(1)	C(1)	C(2)	116.2 (5)
C(8)	C(9)	1.470 (8)	N(2)	C(1)	C(2)	116.6 (5)
C-C(phenyl) range		1.361-1.397	N(3)	C(8)	C(9)	117.0 (6)
C-C(phenyl) mean		1.377	N(4)	C(8)	C(9)	115.5 (6)
C-H range		0.74-1.05	C-C-C range			118.2-121.3
C-H mean		0.94	C-C-H range			109-130

but the major product **6** is easily separated from these side products in good yield (74%). The bicyclic molecule **5** can be regenerated from **6** by treatment with *N,N'*-bis(trimethylsilyl)sulfur diimide.

The reduction of **6** to the dithiatriazine **4** is easily achieved by using triphenylstibine. The product is a yellow microcrystalline solid which decomposes on attempted sublimation at 80 °C/0.01 torr to yield, *inter alia*, S₄N₄. It is remarkably insoluble in most common organic solvents, so that its recrystallization (for X-ray work) proved extremely difficult. The compound is perfectly air-stable in the solid state but appears to be extremely sensitive to oxidation in solution. It can be reoxidized by chlorine to give the 1,3-dichloro compound **6**, and reacts (slowly) with norbornadiene to yield the expected 1,3-adduct **7**. This chemical evidence, coupled with the mass spectral fragmentation pattern and elemental composition of **4** (see Experimental Section), convinced us of the integrity of the CN₃S₂ skeleton, but failed to satisfy our concerns regarding the complete molecular structure. Our previous experience in handling inorganic dithiatriazines such as R₂PN₃S₂ **10**³² and S₃N₃O₂⁻ **11**³³ had led us to anticipate an extremely soluble (in organic media) material with an intense low-energy (~550 nm) π* → π* transition.



An X-ray structural determination on **4** confirmed our suspicion that the 5-phenyl-1,3,2,4,6-dithiatriazine system is dimeric. The solid-state structure described below and the molecular orbital arguments that follow detail the unique structural and electronic features of this compound.

Crystal and Molecular Structure of 4. Crystals of **4** consist of dimeric (PhCN₃S₂)₂ units stacked in a head-to-tail pattern, with the stacks lying approximately along the *yz* diagonal (see Figure 1). Figure 2 illustrates the interdimer phenyl-ring-over-CN₃S₂-ring alignment as viewed perpendicularly to the plane of the heterocyclic ring. This mode of packing is observed in other thiazyl heterocyclic derivatives,^{9,76} although the alternative head-to-head arrangement is also known.³⁴ Adjacent dimer units are related by a center of symmetry and are equally spaced at

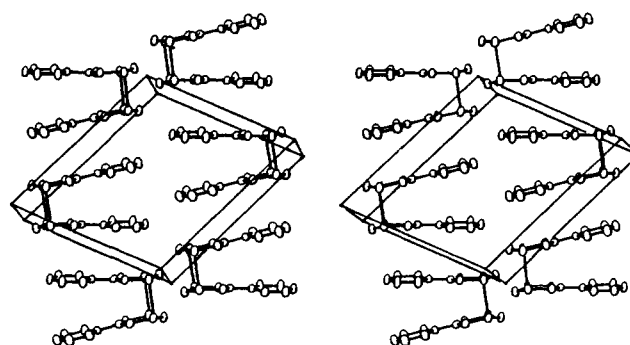


Figure 1. Solid-state packing of (PhCN₃S₂)₂ (**4**) showing the head-to-tail stacking pattern. The origin of the unit cell is in the lowermost corner of the drawing.

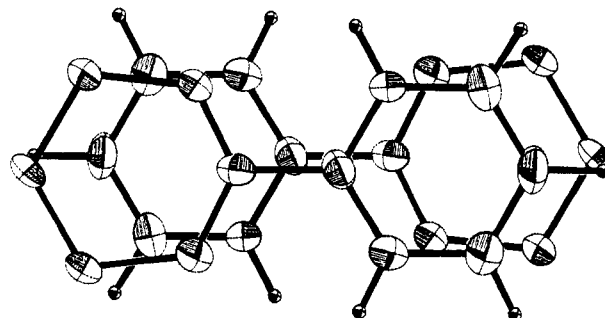


Figure 2. Phenyl-to-heterocycle overlap arrangement between adjacent dimers.

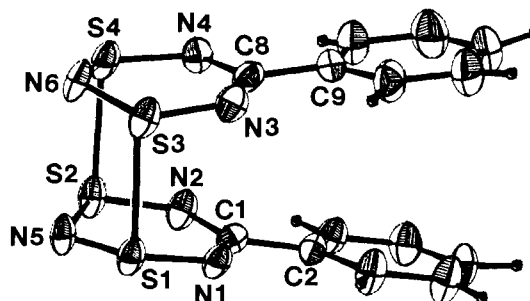


Figure 3. ORTEP drawing of (PhCN₃S₂)₂ (**4**) showing atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are drawn with arbitrary radii.

a phenyl-ring-center to CN₃S₂-ring-center distance of 3.65 Å. This distance is only slightly longer than the sum (3.55 Å) of the van der Waals radii of sulfur and a phenyl ring³⁵ but is significantly

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Table III. Mean Bond Lengths (Å), Valence Angles (deg), and Half-Chair Dihedral Angles τ^a (deg) in 5-Phenyl-1,3,2,4,6-dithiatriazines

	compound			
	4	5	6	7
C-N	1.343	1.336	1.335	1.335
S-N(4, 6)	1.590	1.621	1.591	1.650
S-N(2)	1.624	1.629	1.607	1.641
N-C-N	127.1	129.8	128.4	130.6
C-N-S	122.9	119.8	122.0	117.3
N-S-N	114.0	109.9	111.1	109.8
S-N-S	116.6	111.8	118.4	103.7
τ	16.1	42.9	24.0	52.4
ref	this work	15, 37	38	39

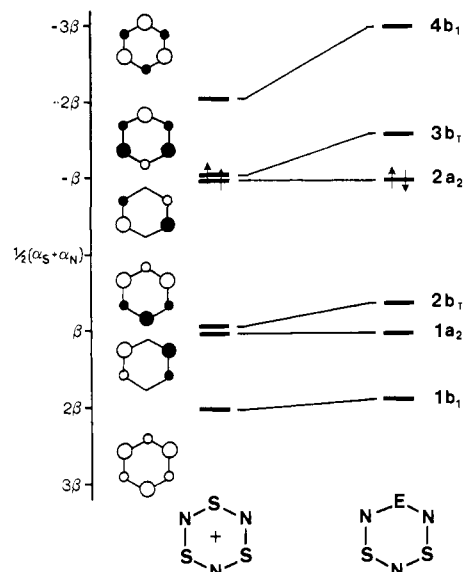
^a τ defines the dihedral angle between the five-atom S-N-C-N-S and three-atom S-N-S planes.

longer than the interplanar separations observed in graphite (3.35–3.37 Å)³⁶ and related heterocyclic compounds, e.g., naphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2,6]thiadiazine (3.40 Å)^{12d} and 1,3,5,2,4-benzotrithiadiazepine (3.29 Å).^{9,34}

An ORTEP drawing of a single (PhCN₃S₂)₂ unit in **4** is shown in Figure 3. The molecule consists of a cofacial arrangement of two CN₃S₂ rings, each of which adopts a half-chair conformation, the unique nitrogens being tipped out of the plane of the remaining five endocyclic atoms (which are both coplanar to within 0.02 Å) to produce dihedral angles of 16.0° and 16.2°. The displacement of the nitrogen atoms is in opposite directions. The two five-atom SNCNS planes are mutually inclined with a dihedral angle of 12.5°, so that while the S-S contacts are 2.524 (3) and 2.530 (3) Å, the phenyl ring centers are separated by 3.73 Å, and the remote C--C distance has opened up to 4.046 Å.

Table III summarizes the pertinent structural parameters of **4** along with the analogous data for the related derivatives **5**, **6**, and **7**.^{37–39} The most noticeable variation is in the half-chair dihedral angle τ (see Table III), which is smallest in **4** and largest in the norbornadiene adduct **7**. The more folded structure of the CN₃S₂ ring in the latter and, to a lesser extent, in **5** can be attributed to the small "bite" of the bridging C-C (and -NSN-) units in these molecules. Similar effects have been observed in other norbornadiene adducts.⁴⁰ The long S-N(2) linkages in **7** and **5** as well as the small endocyclic angles at sulfur and N(2) can also be attributed to a rehybridization occasioned by the presence of the bridge between the two sulfur atoms. We interpret the closer approach to planarity in **4** as compared to **6** as a measure of the weakness of the interaction between the two halves of the dimer; i.e., interannular bonding in **4** is not sufficient to cause a distortion of the π -systems of the two halves (*vide infra*).

Electronic Structures of Dithiatriazine Monomers and Dimers. The molecular structure of **4** described above is markedly different from those of the related inorganic heterocycles **10**³² and **11**³³ that we have prepared and characterized. The latter are monomeric and show no tendency to associate in solution or in the solid state. The electronic factors underlying this structural dichotomy are most easily understood within a simple one-electron HMO context. At this level, the π -electronic structures of the three systems can all be related to that of a single parent, namely the 8 π -electron S₃N₃⁺ cation.⁴¹ A simple π -orbital energy level diagram for this species (assuming D_{3h} symmetry) is shown in Figure 4. With

**Figure 4.** Simple Hückel energy level diagram for a high-spin 8 π -electron S₃N₃⁺ cation ($\alpha_S = \alpha_N - 0.5\beta$) and a perturbed low-spin 8 π -electron EN₃S₂ ring ($\alpha_E = \alpha_S - \beta$). (All β 's are equal.)**Table IV.** Calculated (MNDO) Heats of Formation (kcal/mol) of RCN₃S₂ Derivatives in Singlet ($b_1^2, b_1^2, a_2^2, a_2^2$) and Triplet ($b_1^2, a_2^2, b_1^2, a_2^2, b_1^1$) Configurations

R	singlet	triplet	Δ
H	123.5	108.2	15.3
NH ₂	120.2	108.0	12.2
F	76.6	63.7	12.9
C ₆ H ₅	150.1	135.6	14.5

an 8 π -electron count, S₃N₃⁺ can exist in both singlet and triplet spin states. At the Hückel level, these are degenerate, but the inclusion of electron repulsion will split the degeneracy; following Hund's rule, the triplet will be the most stable. The replacement of one (charged) sulfur atom by a heteroatom, e.g., PR₂ and SO₂⁻ (as in **10** and **11**), will lift the degeneracy of the upper e'' orbitals to produce (in C_{2v} symmetry) a b₁ and a₂ pair. With an electropositive perturbation, as expected here, the 3b₁ orbital will be raised in energy with respect to the 2a₂, which is nodal at the heteroatom site, the extent of the splitting between the two being dependent on the difference in the Coulomb parameters of a sulfur 2p atomic orbital and the appropriate hetero-orbital (3d for phosphorus(V) and sulfur(VI)).⁴² One can therefore imagine a progressive splitting of the 3b₁ and 2a₂ orbitals as a function of the perturbation to a point where the singlet (low spin) configuration becomes more stable than the triplet. This latter situation is certainly observed in **10** and **11**; the 3b₁-2a₂ band gap is easily estimated from their characteristic HOMO-LUMO transition energies.

In the case of a S⁺ ↔ CR replacement, the orbital electronegativity difference is less acute (indeed there has been considerable discussion as to which grouping is more electronegative⁴³), and the energetic balance between a low-spin and high-spin ground state is not easily anticipated by using one-electron arguments. To investigate the energetic difference between the two possible multiplicities, we have carried out MNDO molecular orbital calculations on a model HCN₃S₂ derivative (using a C_{2v} symmetry restriction). Calculations performed within the singlet and triplet options of the MOPAC^{25b} program yield heats of formation (see Table IV) that favor the triplet ($b_1^2, a_2^2, b_1^2, a_2^2, b_1^1$) state over the singlet ($b_1^2, b_1^2, a_2^2, a_2^2$) by 15.3 kcal/mol.⁴⁴ π -Orbital

(42) This simple model assumes only homomorphic interactions at the site of the perturbation.

(43) See, for example: (a) Chivers, T.; Oakley, R. T. *Top. Curr. Chem.* **1982**, 102, 117. (b) Gimarc, B. M.; Trinajstić, N. *Pure Appl. Chem.* **1980**, 52, 1443.

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(38) Graham, J. B.; Cordes, A. W.; Oakley, R. T.; Boerë, R. T. *Acta Crystallogr.*, in press.

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(41) Information on the electronic structure of the S₃N₃⁺ ion can be found in: Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, 101, 4517. See also ref 14b.

Table V. MNDO π -Orbital Energies (ϵ_i , eV), Eigenvector Coefficients (c_i), π -Bond Orders (ρ_π), and π -Charge Densities (q_π) for HCN_3S_2 in Triplet and Singlet^a States

orbital	ϵ_i	c_i			
		C	N(4, 6)	S	N(2)
4b ₁	0.406 (0.876)	-0.729 (-0.768)	0.454 (0.436)	-0.151 (-0.106)	0.104 (0.082)
3b ₁	-5.676 (-2.824)	-0.290 (-0.225)	0.002 (0.018)	-0.443 (-0.469)	0.723 (0.714)
2a ₂	-6.301 (-9.028)		0.558 (0.584)	-0.435 (-0.398)	
2b ₁	-13.024 (-13.330)	0.493 (0.551)	0.352 (0.484)	-0.308 (-0.166)	-0.573 (-0.416)
1a ₂	-13.078 (-12.753)		0.435 (0.398)	0.558 (0.584)	
1b ₁	-15.972 (-16.252)	(0.388) (0.236)	0.413 (0.274)	0.431 (0.492)	0.370 (0.557)
ρ_π		0.661 (0.662)	0.381 (0.109)	0.352 (0.686)	
q_π		0.852 (0.718)	1.278 (1.619)	1.569 (1.539)	1.455 (0.968)

^aData in parenthesis.

energies and distributions for these two states of HCN_3S_2 are summarized in Table V.

In order to probe the sensitivity of the singlet-triplet balance to the nature of the substituent on carbon, we have carried out additional model calculations using a range of ligands with strong inductive and/or conjugative influences; the results are summarized in Table IV. The most notable effect is observed when π -donor ligands, e.g., NH_2 , are present. For this ligand, the singlet/triplet separation is minimized, presumably as a result of a conjugative destabilization of the 3b₁ orbital. However, the energy changes are small, and we conclude that for most monomeric dithiatriazines, the ground state will be a spin triplet. If singlet ground states are to be found, they will probably be associated with strongly electron-releasing ligands bound to carbon.

The structural ramifications of high spin ground states in binary sulfur nitride chemistry are well-known. For example, the cage structure of S_4N_4 is traditionally rationalized in terms of a pseudo-Jahn-Teller distortion⁴⁵ of the planar structure which, in D_{4h} symmetry, would possess a 12π -electron triplet ground state.⁴⁶ In the dithiatriazine structure, no similar distortion coordinate exists, although ring puckering could, in principle, split the accidental degeneracy of the 2a₂ and 3b₁ orbitals. The alternative pathway to a singlet ground state, the one that nature chooses, involves an intermolecular coupling of two triplet units to form a cofacial dimer.

We have investigated the electronic and energetic changes accompanying such a process by carrying out an MNDO calculation on a pair of cofacially aligned HCN_3S_2 molecules (in C_{2v} symmetry). Quantitatively, the MNDO method is not particularly reliable for this system. For example, using a coplanar arrangement of the two HCN_3S_2 rings, the S...S separation optimizes at 2.75 Å, and when the planarity restriction is released, this distance increases to near 6 Å. In addition, the calculated heat of formation of the dimer is considerably more than twice that obtained for the monomer units. As a result of these inadequacies in the theoretical method, the extent of the interaction between the two HCN_3S_2 units, and the strength of the interannular "bond", is hard to establish. This computational difficulty is compounded by an experimental one; we have no evidence for

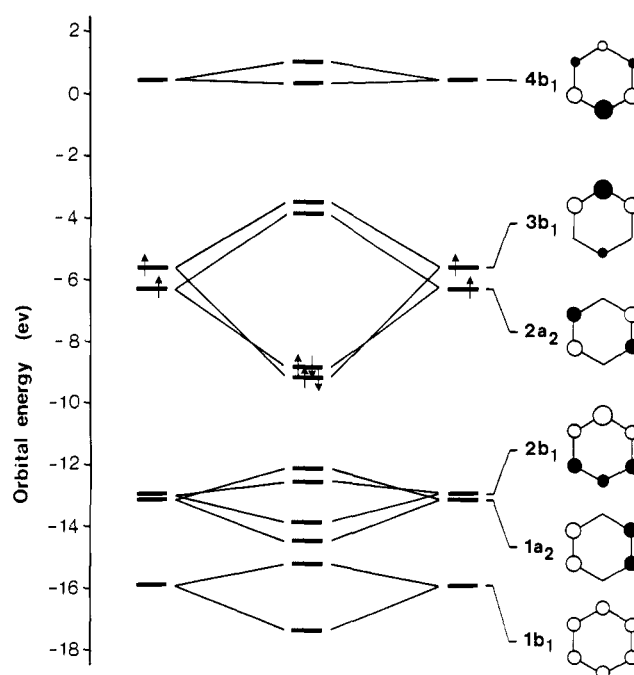


Figure 5. MNDO π -molecular orbital energies and distributions for triplet HCN_3S_2 (see also Table V). Correlation lines illustrate the mixing of the monomer orbitals to form a $(\text{HCN}_3\text{S}_2)_2$ dimer.

the dissociation of **4** into its constituent halves. Attempts to characterize **3** by ESR spectroscopy, and hence establish its spin multiplicity, have been inconclusive. Dilute solutions of **4** in methylene chloride exhibit a five-line signal (with $a_N = 0.50$ mT) characteristic of the NSN^- radical anion, a common decomposition product of many unstable sulfur nitrogen species.⁴⁷ We conclude that if dissociation of **4** to **3** occurs, it is followed rapidly by the decomposition of the latter.

In spite of these difficulties, we can gain some qualitative insight into the electronic makeup of the dimer from our present theoretical results. Figure 5 illustrates the orbital energy changes that occur when two HCN_3S_2 units merge into a dimeric structure (the

(44) Interestingly, the isoelectronic 8π -electron $\text{H}_2\text{C}_2\text{N}_3\text{S}^-$ species (the anion of **1** with $\text{R} = \text{H}$) is a singlet ground state, the triplet lying 28 kcal/mol higher. Boeré, R. T.; Hayes, P. J.; Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Pennington, W. T. *Inorg. Chem.*, submitted for publication.

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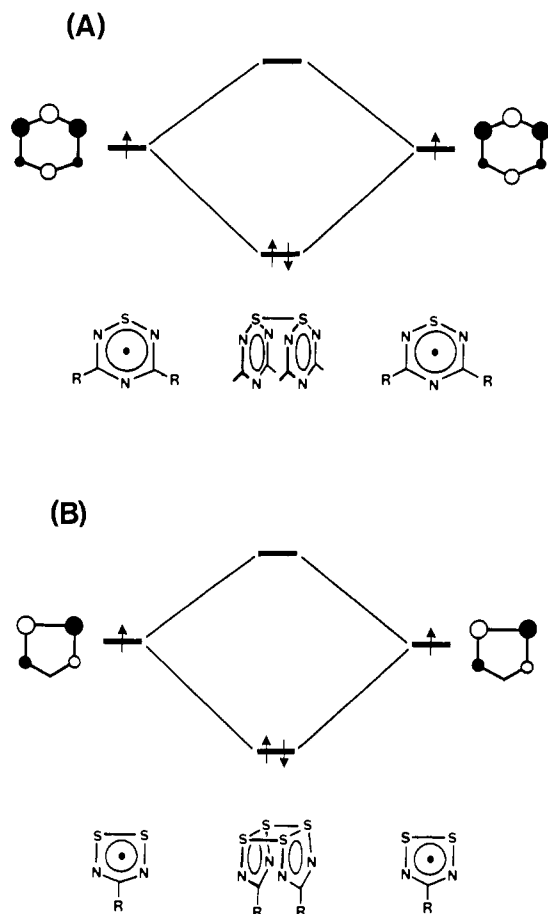


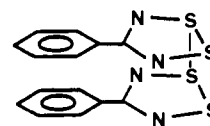
Figure 6. Mixing of SOMO's of (A) $R_2C_2N_3S$ and (B) RCN_2S_2 pairs to form dimer units.

orbital energies of the dimer refer to the optimized model outlined above, with $d(S\cdots S) = 2.75 \text{ \AA}$. As expected, there is a series of pairwise interactions which contribute to the bonding between the halves, but for most of these, there is an approximately equal and opposite contribution from an occupied out-of-phase combination. The net "bond" between the two halves arises from the in-phase overlap of the $3b_1$ and $2a_2$ orbitals on each ring.

This picture is obviously oversimplified, but it does allow a conceptual framework for the structural comparison of **4** with some related compounds. We begin by noting that there is an approximate equivalence in the $S\cdots S$ separations in **4** and those in S_4N_4 (2.59 \AA).⁴⁸ In this latter molecule, there are also two orbitals (net) exhibiting transannular $S\cdots S$ bonding characteristics. On this basis, it is tempting to equate these $S\cdots S$ interactions in valence bond terms to two two-electron bonds. Such a description is entirely illusory; the relevant bonding molecular orbitals are in both cases extremely diffuse and bear little resemblance to the orbital makeup of a typical disulfide bond.

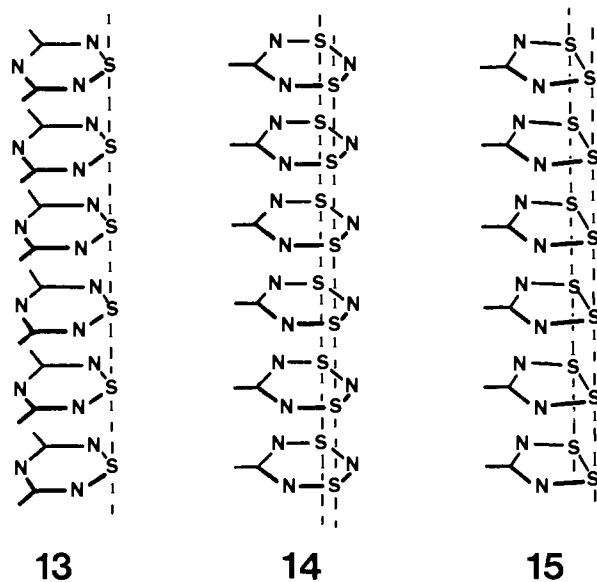
The description of a dithiadiazine dimer as a pair of monomer units bonded together through the weak overlap of their uppermost π -orbitals has analogies elsewhere. In our discussion of the electronic structure of the thiatriazine dimer **2** ($R = Ph$), we stressed the importance of the overlap of the two b_1 SOMO's of the separate halves in bond formation (see Figure 6). Such a description is entirely analogous to that used to interpret the dithionite structure.⁴⁹ For the bis(dithiadiazole) structure **12**, a similar orbital interaction scheme can be developed. The radical halves are, as in **2**, 7π -electron systems, but the SOMO's are of a_2 rather than b_1 symmetry (see Figure 6).^{5,50} It is not surprising that the $S\cdots S$ separation in these dimers varies considerably, from

2.53 \AA in **4** to 2.67 \AA in **2**¹³ and 3.10 \AA in **12**.⁵ The observed value depends on the number of net occupied bonding orbitals (there are two in **4** vs. one in **12**), and the π -orbital coefficients at sulfur in the monomeric building blocks (the orbital diffuseness).



12

These qualitative conclusions provide the basis for considering the potential properties of one-dimensional arrays of heterocyclic thiazenes based on some of the monomer units described above. To be specific, would stacked arrangements such as **13**, **14**, or **15** find applications in the design of molecular metals? We are



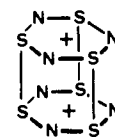
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currently pursuing the synthesis of such systems, paying particular attention to the effect of redox changes on the way in which the monomer units stack, since partial oxidation or reduction would tend to encourage uniform spacing by eliminating Peierls' instabilities. The effect of replacement of sulfur by selenium, and the consequent improvement of interannular overlap, is also being studied.

In addition to the dimeric heterocycles described above, we draw attention to the possibility of intermolecular association in certain binary sulfur nitride species. For example, we noted earlier the analogy, at the one-electron level, between the RCN_3S_2 and $S_3N_3^+$ π -systems. This latter ion is well-known as a dominant fragment in the mass spectral fragmentation pattern of binary SN compounds but has never been structurally characterized. While charge repulsion would mitigate against the association of two gas-phase ions, sufficient interannular binding may occur between two coplanar $S_3N_3^+$ units to stabilize a dimeric $(S_3N_3^+)_2$ dication, e.g., **16**, isostructural with **4**. We suggest this species as a target for theoretical and spectroscopic investigation.



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Summary

An efficient, flexible, and rational synthetic sequence to a range of 5-aryl-1,3,2,4,6-dithiadiazine derivatives has been developed. In contrast to other six-membered EN_3S_2 heterocycles, the

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PhCN₃S₂ system exists as a cofacially bonded dimer, with an S...S separation of 2.53 Å. MNDO calculations on model RCN₃S₂ rings reveal that they possess triplet ground states. The formation of dimeric dithiatriazines arises from the coupling of two such triplets to form a singlet ground state. The structural consequences of modification of the phenyl ring of **4** on the singlet/triplet balance is currently being investigated, as is the effect of redox changes on the stability of the (PhCN₃S₂)₂ structure.

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Registry No. 3, 98990-61-5; 4, 98990-55-7; 5, 98990-56-8; 6, 98990-57-9; 7, 99016-48-5; PhC(N(SiMe₃)₂)NSiMe₃, 24261-90-3; S₃N₃Cl₃, 5964-00-1; Me₃SiNSNSiMe₃, 18156-25-7; HCN₃S₂, 33982-51-3; (HCN₃S₂)₂, 98990-58-0; H₃NCN₃S₂, 98990-59-1; FCN₃S₂, 98990-60-4; triphenylstibine, 603-36-1; norbornadiene, 121-46-0.

Supplementary Material Available: Tables of atom coordinates for hydrogen atoms (S1) and anisotropic thermal parameters (S2) and observed and calculated structure factors (17 pages). Ordering information is available on any current masthead page.

Theoretical Probes of Activated-Complex Structure and Properties: Substituent Effects in Carbonyl Addition

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Abstract: Structures, force fields, vibrational eigenvalues and eigenvectors, potential energies, and Gibbs free energies have been calculated by ab initio quantum-mechanical methods for the reactants, products, and activated complexes of five carbonyl-addition reactions, namely the addition of water, methanol, and ammonia to formaldehyde and the addition of water to acetaldehyde and formyl fluoride. All activated complexes have four-membered ring structures, and the reaction-coordinated eigenvectors show heavy-atom reorganization and proton transfer to be truly concerted in all cases. The structures of the activated complexes are essentially invariant to substitution, the Pauling bond order of the forming carbon-nucleophile bond being 0.42-0.45 and the Pauling bond order of the breaking OH or NH bond being 0.76-0.78 in all cases. Heavy-atom reorganization is thus more advanced than proton transfer in all activated complexes. Potential energies of reaction vary from -4.7 to -17.3 kcal mol⁻¹ and potential energies of activation from 35.6 to 46.2 kcal mol⁻¹. Gibbs free energies of reaction vary from -3.0 to +7.6 kcal mol⁻¹ and Gibbs free energies of activation from 46.4 to 57.6 kcal mol⁻¹. In neither case is there a systematic relationship between rate and equilibrium energetics. Reaction progress of proton transfer is ~25% and that for heavy-atom reorganization ~45% at the activated complex. Both of these features can be derived from the qualitative location of the activated complex on an MAR. This was arrived at by deduction of the parallel effect from the exothermicity of the reactions and of the perpendicular effect from reactant frontier-orbital interactions.

An important current goal of mechanisms chemistry, particularly of the subfield of physical-organic chemistry, is the establishment of generalizations which govern the structure and properties (e.g., energy, charge distribution, force constants) of activated complexes under the influence of experimental variables such as substituents, solvent, etc. Successful generalizations of this kind would allow the a priori calculation of the rate of a reaction under various conditions and would be fundamentally important and practically useful.

Progress in this direction is now being made experimentally by the application to systems of interest of mechanistic probes such as substituent effects, medium effects, and isotope effects. The results are generally interpreted in terms of activated-complex structure. Typically, the slope of a linear free-energy plot or the magnitude of a kinetic isotope effect is used to estimate properties of the activated complex, such as the bond orders of forming or breaking bonds. Then the results of several such studies are used to infer the behavior of the activated complex under different conditions. While this approach has yielded considerable mechanistic information, it relies heavily on empirical relationships and concepts.

Theoretical chemistry has a significant potential for contributing to this area in several ways. The approach chosen here has been

to *simulate* a typical experimental structure-reactivity study of the type described above. The reactions of a series of substituted compounds have been examined, with reactant, activated complex, and product structures and properties being determined in each case. Since free energies of all species are calculated, rate-equilibrium free-energy relationships can be constructed; and since force constants of all species are calculated, isotope effects can be obtained. In contrast to experimental studies, however, the theoretical procedures also yield directly the structures and other properties of all species, including the activated complex. The calculated structures and properties can then be compared with those inferred from free-energy relationships or isotope effects. Thus, this approach has the capacity for testing the empirical relationships, developing the principles behind them, and establishing new and more reliable generalizations for use in interpreting experimental results.

In this paper, we report the response of reactant, product and activated-complex properties to variations of substituent in the prototypical carbonyl-addition reaction we have studied previously.²⁻⁴

Effects of substituents were examined for both the nucleophilic and electrophilic reaction partners. All reactions studied proceed

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