from that of trifluoroethanol for both rate[10] and equilibrium constants; at equilibrium the trifluoroethyl ether is only 3–9 times more stable than the alcohol in the 50% aqueous solvent and is equally stable in 90% water.

This behavior may be described in terms of a relatively large carbon basicity of RO⁻ compared with HO⁻.[15] The reason for this is not clear to us, although it is possible that dispersion interactions stabilize the ether compared with the phenylethyl and aliphatic alcohols. It is not simply a hydrophobic effect, because ether formation is *less* favorable when the water content of the solvent is increased (Tables I and II). It is conceivable that it involves solvophobic interactions with both the fluorocarbon component of the solvent[29] and water.

Registry No. EtOH, 64-17-5; $CH_3O(CH_2)_2OH$, 109-86-4; Cl(CH$_2$)$_2$OH, 107-07-3; Cl$_2$CHCH$_2$OH, 598-38-9; MeOH, 67-56-1; HC≡CCH$_2$OH, 107-19-7; CF$_3$CH$_2$OH, 75-89-8; Me$_2$N-p-C$_6$H$_4$CH(OH)·CH$_3$·HClO$_4$, 94670-01-6; CH$_3$(CH$_2$)$_3$OH, 71-36-3; CH$_3$(CH$_2$)$_2$OH, 71-23-8; Cl(CH$_2$)$_3$OH, 627-30-5; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OEt·HClO$_4$, 94670-03-8; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$OMe·HClO$_4$, 94670-05-0; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$Cl·HClO$_4$, 94670-07-2; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$CHCl$_2$·HClO$_4$, 94670-09-4; Me$_2$N-p-C$_6$H$_4$CH-(CH$_3$)OMe·HClO$_4$, 94670-11-8; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$≡CH·HClO$_4$, 94670-13-0; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_3$CH$_3$·HClO$_4$, 94670-15-2; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$CH$_3$·HClO$_4$, 94670-17-4; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$Cl·HClO$_4$, 94670-19-6; MeO-p-C$_6$H$_4$CH(CH$_3$)OH, 3319-15-1; MeO-p-C$_6$H$_4$CH(CH$_3$)OEt, 67233-95-8; MeO-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$OMe, 94670-20-9; MeO-p-C$_6$H$_4$CH-(CH$_3$)O(CH$_2$)$_2$Cl, 94670-21-0; MeO-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$CHCl$_2$, 94670-22-1; MeO-p-C$_6$H$_4$CH(CH$_3$)OMe, 77525-91-8; MeO-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$C≡CH, 94670-23-2; MeO-p-C$_6$H$_4$CH(CH$_3$)O-(CH$_2$)$_3$Cl, 94670-24-3; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OH, 5338-94-3; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OEt, 94670-02-7; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O-(CH$_2$)$_2$OMe, 94670-04-9; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)O(CH$_2$)$_2$Cl, 94670-06-1; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OMe, 94670-10-7; Me$_2$N-p-C$_6$H$_4$CH-(CH$_3$)O(CH$_2$)$_3$CH$_3$, 94670-14-1; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$CF$_3$·HClO$_4$, 94670-30-1; MeO-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$CF$_3$, 94670-31-2; Me$_2$N-p-C$_6$H$_4$CH(CH$_3$)OCH$_2$CF$_3$, 94670-29-8; 1-(4-methoxy-3-nitrophenyl)ethanol, 67223-02-3; 1-(4-methoxy-3-nitrophenyl)ethyl ethyl ether, 94669-95-1; 1-(4-methoxy-3-nitrophenyl)ethyl 2-methoxyethyl ether, 94669-96-2; 1-(4-methoxy-3-nitrophenyl)ethyl 2-chloroethyl ether, 94669-97-3; 1-(4-methoxy-3-nitrophenyl)ethyl 2,2-dichloroethyl ether, 94669-98-4; 1-(4-methoxy-3-nitrophenyl)ethyl methyl ether, 94669-99-5; 1-(4-methoxy-3-nitrophenyl)ethyl prop-2-yn-1-yl ether, 94670-00-5; 3-bromo-α-methyl-4-methoxybenzenemethanol, 94670-25-4; 1-(3-bromo-4-methoxyphenyl)ethyl ethyl ether, 94670-26-5; 1-(3-bromo-4-methoxyphenyl)ethyl methyl ether, 94670-27-6; 1-(4-methoxy-3-nitrophenyl)ethyl 2,2,2-trifluoroethyl ether, 94670-28-7; 1-(3-bromo-4-methoxyphenyl)-ethyl 2,2,2-trifluoroethyl ether, 94670-32-3.

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Preparation and Dimerization of 1,2,4,6-Thiatriazinyl Radicals: Crystal and Molecular Structure of Bis(3,5-diphenyl-1,2,4,6-thiatriazine)

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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, N1G 2W1 Canada, and the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. Received September 7, 1984

Abstract: The reduction of Ph$_2$C$_2$N$_3$SCl, prepared from the reaction of benzamidine with S$_3$N$_3$Cl$_3$, with triphenylantimony yields the 3,5-diphenyl-1,2,4,6-thiatriazinyl radical Ph$_2$C$_2$N$_3$S·, whose ESR signal in CH$_2$Cl$_2$ consists of a seven-line pattern with equal hyperfine coupling constants to all three nitrogen atoms (a_N = 0.397 mT, g = 2.0059). In the solid state the radical forms a dimer, whose crystal structure has been determined by X-ray diffraction. Crystals of (Ph$_2$C$_2$N$_3$S)$_2$ are triclinic, space group $P\bar{1}$, a = 8.894 (3) Å, b = 11.058 (3) Å, c = 12.814 (5) Å, α = 81.76 (2), β = 86.75 (3), γ = 76.00 (2)°, V = 1209.9 Å^3, and Z = 2. The structure was solved by direct methods and refined by Fourier and full-matrix least-squares techniques to give a final R = 0.050 and R_w = 0.056 for 1125 reflections with $I > 2\sigma I$. The solid-state structure of the dimer consists of a pair of cofacial Ph$_2$C$_2$N$_3$S rings with a dihedral angle of 14° between their respective mean planes. The closest interring contact is between two sulfur atoms (2.666 (3) Å). The electronic structures of the radical and the dimer are discussed in the light of MNDO molecular orbital calculations on related model compounds.

The possibility of emulating the electronic properties of the (SN)$_x$ polymer[2] by incorporating carbon atoms into conjugated sulfur–nitrogen chains has provided a stimulus for research in organothiazyl chemistry. As a result the preparation and characterization of a variety of novel heterocyclic thiazyl compounds have recently been reported.[3–8] In principle at least these compounds combine the structural stability of carbocyclic π systems with the interesting redox properties of sulfur–nitrogen linkages. In this latter context the generation of planar ring systems which can exist in a variety of stable oxidation states (cation, anion, and radical) is a particularly appealing target. The importance of such

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a feature in the design of one-dimensional conductors has been pointed out by Haddon,[9] and several attempts to exploit this concept have been described.[10]

As a part of our work in this area, we have discovered that the reduction of 1-chloro-3,5-diphenyl-1,2,4,6-thiatriazine (1) with triphenylantimony yields the stable 3,5-diphenyl-1,2,4,6-thiatriazinyl radical (2) (eq 1).[11] In the solid state, the radical forms
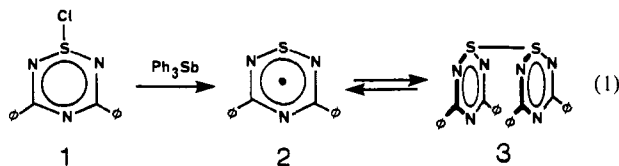
a sulfur–sulfur bridged dimer, 3. We report herein the characterization of the $Ph_2C_2N_3S\cdot$ radical and the crystal and molecular structure of its dimer 3. The ESR spectral parameters of 2 and the solid-state structure of 3 are discussed on the basis of molecular orbital (MNDO) calculations on a variety of model compounds.

Experimental Section

Starting Materials and General Procedures. $S_3N_3Cl_3$[12] was prepared from S_4N_4[13] and SO_2Cl_2 by the literature method. Benzamidine was liberated from benzamidine hydrochloride hydrate (Aldrich) by treatment with 5 M NaOH and extraction into diethyl ether and was sublimed in vacuo prior to use. Acetonitrile (Fisher, HPLC grade) was doubly distilled from CaH_2 and P_2O_5. Carbon tetrachloride (Fisher, technical) was distilled from P_2O_5. Triphenylantimony (Aldrich) was recrystallized from acetonitrile. Infrared spectra were recorded on Nujol mulls (CsI cells) on a Perkin-Elmer 1330 grating spectrophotometer. Chemical analyses were performed by MHW laboratories, Phoenix, AZ. All melting points were measured on a Gallenkamp melting point apparatus and were uncorrected. Mass spectra were obtained by using a VG 7070 EF spectrometer at 70 eV, samples being admitted through conventional inlet systems. All preparative manipulations and reactions were carried out under an atmosphere of nitrogen. ESR spectra (*X* band) were recorded on a Varian 104 ESR spectrometer on degassed solutions in methylene chloride.

Preparation of $Ph_2C_2N_3SCl$. Benzamidine (5.622 g, 46.9 mmol) was combined with $S_3N_3Cl_3$ (4.578 g, 18.7 mmol) and acetonitrile (125 mL) in a side-armed flask and the mixture heated at reflux for 16 h. The contents of the flask were then filtered (hot), and the filtrate was cooled in an ice bath to yield a yellow crystalline solid (weight 5.88 g). Some S_4N_4 (a byproduct) was removed from this solid by a careful overnight sublimation at 70 °C/10^{-2} torr. The residual solid was extracted with hot carbon tetrachloride and the extract then filtered (hot) and reduced to dryness in vacuo (this process removes the coproduced $PhCN_2S_2Cl$[14]). Recrystallization of the residue from acetonitrile yielded yellow moisture-sensitive needles of $Ph_2C_2N_3SCl$ (2.28 g, 7.92 mmol); mp 162–167 °C; IR 3060 (w), 1595 (s), 1465 (vs, br), 1300 (w), 1170 (m), 1160 (s), 1120 (m), 1100 (s), 1080 (s), 1020 (m), 1000 (m), 975 (s), 940 (m), 850 (s), 805 (m), 795 (w), 730 (vs), 680 (vs), 620 (s), 610 (s), 545 (s), 500 (w), 400 (m), 380 (m), 250 (m), 230 (m) cm^{-1}; mass spectrum, *m/e* 252 ($Ph_2C_2N_3S^+$, 34%), 149 ($PhCN_2S^+$, 21%), 103 ($PhCN^+$, 50%), 77 (Ph^+, 19%), 46 (SN^+, 100%). Anal. Calcd for $C_{14}H_{10}N_3SCl$: C, 58.4; H 3.5; N, 14.6; Cl, 12.3. Found: C, 57.7; H, 3.8; N, 14.7; Cl, 12.7.

Preparation of $(Ph_2C_2N_3S)_2$. Solid triphenylantimony (0.52 g, 1.48 mmol) was added to a slurry of $Ph_2C_2N_3SCl$ (0.829 g, 2.88 mmol) in acetonitrile (30 mL). A dark brown microcrystalline precipitate of $(Ph_2C_2N_3S)_2$ (0.621 g, 1.23 mmol, 85%) was filtered from the mixture after 10 min. The product so obtained was analytically pure but was recrystallized for X-ray crystallographic purposes from carefully (five freeze–pump–thaw cycles) degassed acetonitrile as black plates: mp

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Table I. Crystallographic Data

formula	$S_2N_6C_{28}H_{20}$
fw	504.6
cryst. syst.	triclinic
space group: molecules/cell	$P\bar{1}$: 2
a, Å	8.894 (3)
b, Å	11.058 (3)
c, Å	12.814 (5)
α, deg	81.76 (2)
β, deg	86.75 (3)
γ, deg	76.00 (2)
V, Å^3	1209.9
calcd density, g cm^{-3}	1.39

178–181 °C; IR 3060 (w), 1610 (vw), 1590 (m), 1460 (vs, br), 1340 (w), 1210 (m), 1170 (s), 1130 (m), 1065 (s, br), 1020 (s), 965 (m), 775 (vs), 680 (vs), 615 (s), 520 (s), 340 (w) cm^{-1}; mass spectrum, *m/e* 252 ($Ph_2C_2N_3S^+$, 45%), 149 ($PhCN_2S^+$, 27%), 103 ($PhCN^+$, 50%), 77 (Ph^+, 9%), 46 (SN^+, 100%). Anal. Calcd for $C_{28}H_{20}N_6S_2$: C, 66.7; H, 4.0; N, 16.7; S, 12.7. Found: C, 66.3; H, 4.2; N, 16.7; S, 12.5.

X-ray Measurements on $(Ph_2C_2N_3S)_2$ (3). The black opaque crystals of the dimer 3 are soft and crumbly with terraced faces and internal cavities. Many crystals were examined, and data sets were collected on three different crystals.[15] The data used for this report have a typical paucity of observed reflections. The refinement, the final *R*, the internal consistency of related parameters, and the reasonableness of the thermal ellipsoids were a pleasant surprise in view of the apparent crystal quality and the small data set. A crystal of approximate dimensions 0.10 × 0.18 × 0.42 mm, mounted on a glass fiber, was used for data collection on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. A least-squares fit of the diffractometer setting angles for 25 carefully centered reflections (31° < 2θ < 37°) gave the unit cell parameters listed in Table I.

Reflections were measured using ω – 2θ scans for 2θ from 2° to 50° (*h* = –9 to 0, *k* = –11 to 11, *l* = –13 to 13). The scan range was (1.00 + 0.35 tan θ)°, and the scan speed varied from 20° to 4°/min. Of the 3781 unique reflections measured, 1125 had *I* > 2σ*I* and were used in the refinement. Data were corrected for Lorentz and polarization effects, and the analytical absorption correction gave corrections from 0.952 to 0.978 (μ = 2.4 cm^{-1}). Periodic measurement of the intensities of three reflections indicated a crystal and electronic stability of +1.4%. The *R* value for the duplicate data merge was 0.025.

The structure was solved by direct methods (MULTAN 11/82)[16] and refined by full-matrix least-squares techniques. The solution was made difficult by the many parallel hexagon rings (the chicken wire problem). It was solved first in space group $P1$ by using Fourier maps phased by one molecule which was oriented according to $P\bar{1}$ E maps of an incorrect packing arrangement. Hydrogen atoms located in idealized positions (C–H = 0.95 Å) with isotropic thermal parameters of 1.2 times those of the carbon to which they were attached were included in the calculation of structure factors. The final cycle of refinement based on $|F_o^2 - F_c^2|$ included positional and anisotropic thermal parameters for all non-hydrogen atoms. The final *R* = 0.050 and R_w = 0.056.[17] The weighting scheme of $w = [\sigma^2 F + 0.07F^2]^{-1}$ where σ*F* was derived from counting statistics gave *F*/σ values independent of θ or *F*. The goodness of fit[17] was 1.13. In the final cycle of refinement, the maximum shift/error was 0.07. The final difference map had a maximum value of 0.18 e$^-$/Å^3. The atomic scattering factors for neutral atoms were those of Cromer and Waber,[18] and the real and imaginary dispersion corrections were those of Cromer.[19] The computer programs used were those pro-

(15) The dimer also crystallizes in the monoclinic space group $P2_1/n$ with *a* = 11.360 (3) Å, *b* = 10.962 (3) Å, *c* = 19.415 (7) Å, β = 99.94 Å, (2)°, *Z* = 4. Only a few low quality monoclinic crystals were found. The best of these yielded 1051 observed reflections which were sufficient for a solution of the structure but did not support a refinement below an *R* of 0.14. The average of each type of bond distance and angle in the dimer was within 2σ's of the corresponding value for the triclinic crystal. The packing in the monoclinic cell was also void of any special intermolecular alignment.

(16) Main, P. MULTAN 11/82, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. University of York, England.

(17) (a) $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. (b) G.O.F. = $[w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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(19) Cromer, D. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

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Table II. Final Atom Coordinates (for Non-Hydrogen Atoms) and $B_{eq}{}^a$ Values for $(Ph_2C_2N_3S)_2$

atom	x	y	z	B, $Å^2$
S(1)	0.0811 (2)	0.0280 (2)	0.2039 (2)	4.53 (5)
S(2)	-0.1321 (2)	0.1398 (2)	0.0593 (2)	4.33 (5)
N(1)	0.0557 (6)	-0.1112 (5)	0.2048 (5)	4.1 (2)
N(2)	-0.1351 (6)	-0.0798 (5)	0.3449 (4)	4.1 (2)
N(3)	-0.0117 (6)	0.0923 (5)	0.3035 (5)	4.3 (2)
N(4)	-0.1845 (6)	0.0141 (5)	0.0409 (4)	3.9 (2)
N(5)	-0.3975 (6)	0.0581 (5)	0.1663 (4)	3.8 (2)
N(6)	-0.2566 (6)	0.2203 (5)	0.1373 (5)	4.2 (2)
C(1)	-0.0486 (8)	-0.1461 (6)	0.2730 (6)	3.9 (2)
C(2)	-0.0694 (8)	-0.2745 (7)	0.2730 (5)	3.9 (2)
C(3)	0.0162 (9)	-0.3506 (7)	0.2028 (7)	5.8 (2)
C(4)	-0.004 (1)	-0.4689 (8)	0.1994 (7)	7.2 (3)
C(5)	-0.1069 (9)	-0.5162 (7)	0.2646 (7)	6.5 (3)
C(6)	-0.1919 (9)	-0.4430 (7)	0.3336 (7)	6.7 (3)
C(7)	-0.1751 (9)	-0.3242 (7)	0.3381 (7)	5.8 (2)
C(8)	-0.1089 (7)	0.0315 (6)	0.3580 (6)	3.6 (2)
C(9)	-0.1962 (9)	0.0965 (6)	0.4437 (5)	3.4 (2)
C(10)	-0.3111 (9)	0.0506 (7)	0.5010 (6)	5.4 (2)
C(11)	-0.3968 (8)	0.1149 (7)	0.5787 (7)	6.4 (2)
C(12)	-0.3630 (9)	0.2195 (7)	0.6010 (6)	5.7 (2)
C(13)	-0.248 (1)	0.2669 (7)	0.5479 (7)	6.1 (2)
C(14)	-0.1638 (8)	0.2022 (7)	0.4692 (6)	5.1 (2)
C(15)	-0.3092 (7)	-0.0107 (6)	0.0977 (5)	3.5 (2)
C(16)	-0.3547 (7)	-0.1267 (6)	0.0798 (5)	3.5 (2)
C(17)	-0.2661 (8)	-0.2153 (7)	0.0208 (6)	5.2 (2)
C(18)	-0.3136 (9)	-0.3215 (7)	0.0079 (7)	6.4 (2)
C(19)	-0.4491 (8)	-0.3411 (7)	0.0546 (7)	5.6 (2)
C(20)	-0.5386 (8)	-0.2533 (7)	0.1112 (6)	5.4 (2)
C(21)	-0.4909 (8)	-0.1479 (6)	0.1254 (6)	4.3 (2)
C(22)	-0.3716 (7)	0.1694 (6)	0.1785 (6)	3.8 (2)
C(23)	-0.4861 (7)	0.2467 (6)	0.2458 (5)	3.5 (2)
C(24)	-0.6124 (8)	0.2046 (7)	0.2879 (6)	5.2 (2)
C(25)	-0.7184 (8)	0.2757 (7)	0.3516 (7)	6.4 (3)
C(26)	-0.7011 (9)	0.3867 (7)	0.3708 (7)	6.4 (3)
C(27)	-0.5782 (9)	0.4328 (8)	0.3281 (8)	8.0 (3)
C(28)	-0.4718 (8)	0.3602 (7)	0.2659 (7)	6.0 (2)

$^a B_{eq}$ = isotropic B values equivalent to the anisotropic ellipsoids = $^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$.

vided by the Enraf-Nonius Structure Determination Package. Atom coordinates for the non-hydrogen atoms of **3** are given in Table II, and selected bond and angle information is provided in Table III. Tables containing coordinates of the hydrogen atoms (S1), additional bond and angle data (S2), and anisotropic thermal parameters (S3) have been deposited as supplementary material.

Theoretical Method and Models. The MNDO (modified neglect of diatomic overlap) method[20] and the DFP geometry optimizing algorithm[21] have been used extensively for the study of the conformational characteristics of binary thiazyl compounds and related derivatives. The method is recognized to be somewhat deficient in assessing interactions between higher valent sulfur centers[22] but has, in many cases, provided reliable predictions of ground-state geometries. Restricted Hartree–Fock (RHF) open-shell calculations (half-electron model) were carried out on a planar $H_2C_2N_3S\cdot$ species (with full geometry optimization within the C_{2v} symmetry) as a model for the radical **2**. Calculations pertaining to the dimer **3** were performed on two cofacial $H_2C_2N_3S$ units, using the geometrical parameters obtained from the free radical calculations. The sulfur–sulfur distance was set at 2.66 Å, and the dihedral angle between the planes of the two half-molecules was fixed at 16° (cf. the crystal structure).
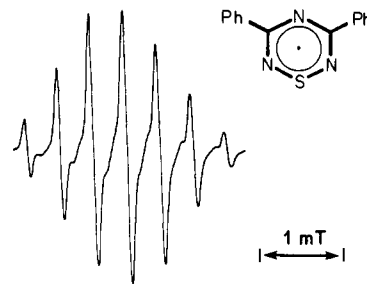
Results and Discussion

Preparation of $Ph_2C_2N_3SCl$ (1). 1,2,4,6-Thiatriazines are known with a wide range of substituents (at sulfur and carbon). For example, derivatives with alkyl or aryl groups in the 1-, 3-, and 5-positions have been prepared by the reaction of N-halo-amidines with thiolates or N-sulfenylamidines.[23] The fully

Figure 1. ESR spectrum of the $Ph_2C_2N_3S\cdot$ radical in methylene chloride.

chlorinated compound $Cl_3C_2N_3S$ can be prepared from sodium dicyanoamide and thionyl chloride,[24] and mixed derivatives, e.g. 1-chloro-3-phenyl-5-(trichloromethyl)-1,2,4,6-thiatriazine, are accessible via ring closure reactions between imidoylamidines and sulfur dichloride.[25] The method reported here, which involves the reaction of benzamidine with $S_3N_3Cl_3$ (eq 2), represents a convenient and apparently versatile route to 1-chloro-3,5-diaryl derivatives. The major side product of the reaction (other than
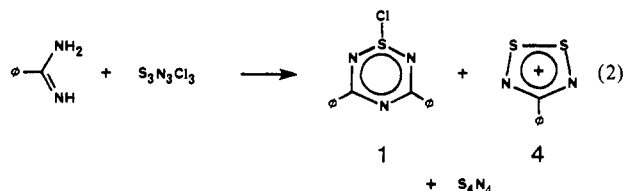
amidine salts and S_4N_4) is the phenyldithiadiazolium chloride **4**,[14] but this can be easily separated from the product by extraction with carbon tetrachloride (in which **4** is insoluble). We note that **1** is not produced in the reaction of benzonitrile with $S_3N_3Cl_3$. In this latter reaction **4** is the sole product.[14]

Reduction of $Ph_2C_2N_3SCl$ and the ESR Spectrum of $Ph_2C_2N_3S\cdot$ (2). Reduction of $Ph_2C_2N_3SCl$ (**1**) with triphenylantimony in deoxygenated methylene chloride yields a yellow solution which exhibits a strong and persistent ESR signal (Figure 1) whose appearance is consistent with that expected for the free radical $Ph_2C_2N_3S\cdot$(**2**), in which hyperfine coupling constants to all three nitrogen atoms are equal (a_N = 0.397 mT). No additional fine structure due to spin coupling to the protons on the phenyl rings is observed. This is in contrast to the spin distribution found in the 2,4,6-triphenylthiopyranyl radical **5**,[26] where significant coupling to the phenyl protons is seen. The deviation of the g

5

value of **2** (2.0059) from the free-electron figure (2.0023) is indicative of a substantial spin density on the sulfur atom (the only atom which is sufficiently heavy to induce a spin–orbit coupling effect). Indeed the g value observed in **2** is siimilar to that reported for the $SO_2{}^-\cdot$ radical (2.0061–2.0057).[27] The ESR results thus suggest that the spin orbital in which the unpaired electron resides is distributed equally over the N2,6 and the N4 nitrogens, with a large contribution also coming from the sulfur

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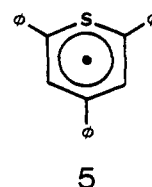
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Table III. Selected Bond (Å) and Angle (deg) Data for (Ph$_2$C$_2$N$_3$S)$_2$

atom	atom 2	distance	atom 1	atom 2	atom 3	angle
S(1)	S(2)	2.666 (3)	S(2)	S(1)	N(1)	95.7 (3)
S(1)	N(1)	1.602 (6)	S(2)	S(1)	N(3)	96.9 (2)
S(1)	N(3)	1.627 (6)	S(1)	S(2)	N(6)	97.0 (3)
S(2)	N(4)	1.614(6)	S(1)	S(2)	N(4)	96.6 (3)
S(2)	N(6)	1.624 (6)	N(1)	S(1)	N(3)	110.7 (4)
N(1)	C(1)	1.316 (9)	N(4)	S(2)	N(6)	110.8 (3)
N(2)	C(1)	1.34 (1)	S(1)	N(1)	C(1)	117.2 (6)
N(2)	C(8)	1.34 (1)	C(1)	N(2)	C(8)	119.2 (7)
N(3)	C(8)	1.32 (1)	S(1)	N(3)	C(8)	116.2 (6)
N(4)	C(15)	1.34 (1)	S(2)	N(4)	C(15)	116.7 (6)
N(5)	C(15)	1.33 (1)	C(15)	N(5)	C(22)	119.6 (7)
N(5)	C(22)	1.33 (1)	S(2)	N(6)	C(22)	116.6 (6)
N(6)	C(22)	1.32 (1)	N(1)	C(1)	N(2)	127.7 (8)
C(1)	C(2)	1.47 (1)	N(1)	C(1)	C(2)	116.3 (9)
C(8)	C(9)	1.47 (1)	N(2)	C(1)	C(2)	115.9 (9)
C(15)	C(16)	1.48 (1)	N(2)	C(8)	N(3)	128.1 (8)
C(22)	C(23)	1.47 (1)	N(2)	C(8)	C(9)	117.7 (8)
			N(3)	C(8)	C(9)	114.2 (7)
			N(4)	C(15)	N(5)	127.5 (8)
			N(4)	C(15)	C(16)	115.8 (8)
			N(5)	C(15)	C(16)	116.8 (8)
			N(5)	C(22)	N(6)	128.3 (8)
			N(5)	C(22)	C(23)	116.3 (8)
			N(6)	C(22)	C(23)	115.5 (8)
			C(22)	C(23)	C(24)	119.6 (8)
			C(22)	C(23)	C(28)	122.1 (8)
			C(24)	C(23)	C(28)	118.3 (8)
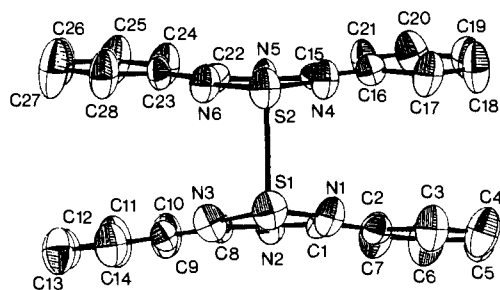
Figure 2. ORTEP drawing of (Ph$_2$C$_2$N$_3$S)$_2$ (50% probability ellipsoids) showing atom numbering scheme.

atom. As a result of the electronegative potential exerted by the C$_2$N$_3$S ring, spin delocalization onto the phenyl rings does not occur to any measureable extent.

Molecular Structure of (Ph$_2$C$_2$N$_3$S)$_2$ (3). Reduction of **2** in acetonitrile yields a microcrystalline precipitate of **3** which can be recrystallized as flat plates from carefully degassed acetonitrile. The crystal structure of this material (which is diamagnetic at room temperature) reveals discrete pairs of thiatriazine rings linked in a cofacial fashion (Figure 2); there are no unusually short contacts between dimers. Individually the two C$_2$N$_3$S rings exhibit shallow boat conformations (Figure 3). In one ring (that containing S1), the sulfur atom and the remote nitrogen atom are displaced 0.135 (2) and 0.048 (6) Å from the mean plane of the central four atoms, which are themselves coplanar to within 0.006 (7) Å. In the other ring (containing S2), the corresponding displacements are 0.074 (2) and 0.053 (5) Å, the remaining atoms being coplanar to within 0.010 (7) Å. Overall, the two rings are planar to within 0.081 (6) and 0.051 (5) Å, respectively, and their two mean planes intersect with a dihedral angle of 14°. The shortest contact is 2.666 (3) Å for S1–S2,[28] although all pairwise contacts are within the appropriate van der Waals' separation. The two C$_2$N$_3$S rings are perfectly eclipsed; i.e., two adjacent atoms from one ring and the corresponding atoms from the other form a planar arrangement (to within 1σ). Torsion angles between
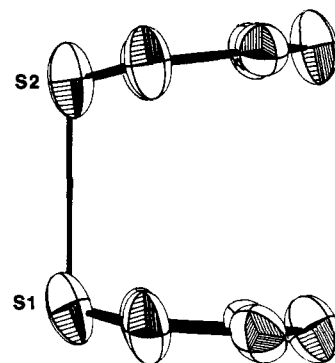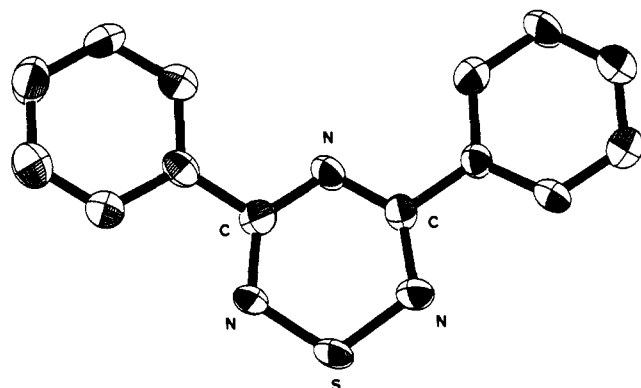
Figure 3. (a) A View (30% probability ellipsoids) of one of the Ph$_2$C$_2$N$_3$S halves and (b) a side-on view of a pair of C$_2$N$_3$S rings (50% probability ellipsoids) in (Ph$_2$C$_2$N$_3$S)$_2$.

the phenyl rings and the C$_2$N$_3$S rings range from 3.8° to 11.4°.

The appearance of the dimer **3**, as outlined above, is reminiscent of the dithionite structure **6**.[29] In the solid state (as its sodium salt), this anion exists as a pair of SO$_2^-$ radicals connected by a long (2.39 Å) S–S linkage. Quite recently a related structure, namely that of Se$_2$I$_4^{2+}$ (**7**), has been reported.[30] Like **3**, both of these structures are characterized by an eclipsed arrangement of

(28) The dimerization of **2** through sulfur differs from thiopyranyl radicals, which dimerize through carbon at the 4-positions. See: Yoshida, Z-i.; Shigeo, Y.; Toyanari, S.; Osanu, K. *Tetrahedron Lett.* **1971**, *43*, 3999. In the thiatriazinyl radical **2**, the 4-position is occupied by a nitrogen atom and, as has been pointed out elsewhere (see ref 8b), N–N bond formation is less thermodynamically favored than C–C.

(29) Dunitz, J. *Acta Crystallogr.* **1956**, *9*, 579.
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Hayes et al.
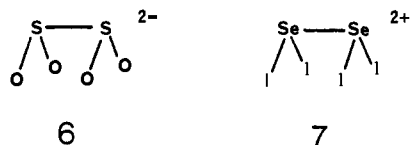
the ligands bound to sulfur (or selenium) and an unusually shallow dihedral angle between the planes of the two half-molecules. However, perhaps the most useful structural analogy that can be drawn is with the transannular S–S interactions observed in binary sulfur nitrides. The nature of these latter interactions, which range from 2.45 to 2.65 Å (e.g., 2.59 Å in S_4N_4),[31] has been the subject of much debate; i.e., is there a bond at all? The issue has been highlighted by the preparation and characterization of a range of heterocyclic derivatives of the type $R_2C_2N_4S_2$,[4] whose structures are either planar **8** or puckered **9** depending on the nature of the R group. Recent theoretical studies[22c,32] on molecules of this type
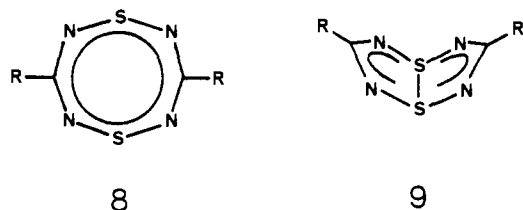
have clarified the electronic criteria which govern the structural dichotomy. The equilibrium between **2** and **3** is analogous to this dichotomy, and similar electronic arguments should be applicable in understanding the apparent weakness of the S–S bond in **3**. In order to develop these ideas, we have carried out a series of MNDO molecular orbital calculations on model compounds related to **2** and **3**.

Electronic Structure of $H_2C_2N_3S$· and $(H_2C_2N_3S)_2$. The length of the S–S bond in **3** and the susceptibility of the dimer to dissociate in solution into its constituent radicals indicate that the S–S interaction is in no way comparable energetically to the S–S bond in an ordinary disulfide molecule, e.g., RSSR. Indeed the dissociation energy of disulfide bonds (50.9 kcal/mol)[33] ranks among the highest for homonuclear linkages. The electronic structure of the dimer, in particular the nature of the S–S interaction, can best be analyzed by considering first the electronic makeup of the simple radical $H_2C_2N_3S$·. The molecular orbital manifold of the dimer can then be characterized in terms of the weak orbital interactions which develop when two $H_2C_2N_3S$· radicals approach one another in a face-to-face fashion.

RHF (open shell) MNDO calculations on a $H_2C_2N_3S$· model (with full geometry optimization within C_{2v} symmetry) confirm that the species is a π radical with a $^2B_1$ ground state. There are three doubly occupied π orbitals ($1b_1$, $1a_2$, and $2b_1$), all of which are bonding distributions (see Table IV). However, for present purposes the orbital of concern is the SOMO $3b_1$, which is an antibonding distribution localized primarily over the NSN region but with a substantial contribution being made by the $2p_z$ orbital of the unique nitrogen. Indeed the nearly equal eigenvector coefficients at the chemically distinct nitrogen (and hence the charge density distribution for the unpaired electron) correlate quite well with the observed coupling constants in $Ph_2C_2N_3S$·, which are essentially identical. The large eigenvector coefficient of the sulfur $2p_z$ orbital is likewise consistent with the high *g* value of **2**.

The cofacial approach of two radical units to form the dimer leads to mixing of the π orbitals of the individual components.

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

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(33) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Table IV. Eigenvalues (ϵ_i) and Eigenvector Coefficients (c_i) of π-Molecular Orbitals (MNDO) of $H_2C_2N_3S$

orbital	ϵ_i, eV	c_i			
		S1	N2,6	C3,5	N4
$4b_1$	1.378	0.144	−0.308	0.520	−0.498
$2a_2$	−0.676		−0.414	0.574	
$3b_1$	−5.870	0.591	−0.443	−0.113	0.482
$2b_1$	−12.411	−0.644	−0.169	0.280	0.609
$1a_2$	−12.623		0.574	0.414	
$1b_1$	−15.818	0.464	0.424	0.371	0.386
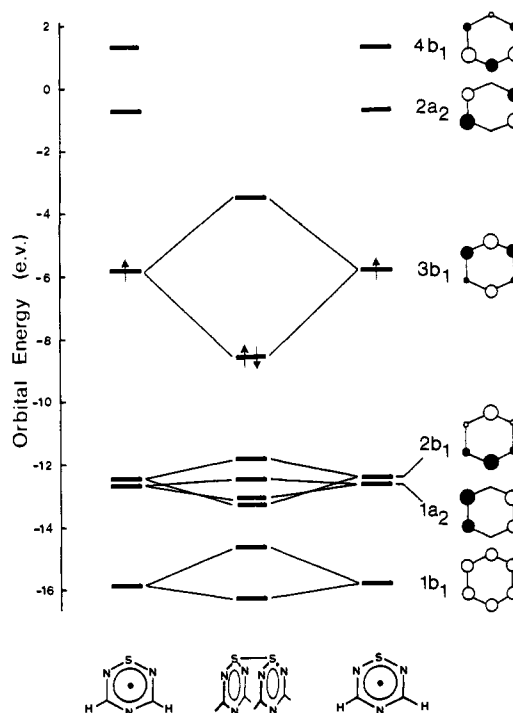
Figure 4. Molecular orbital energies and distributions (also see Table IV). Correlation lines illustrate the mixing of the radical orbitals into those of the dimer $(H_2iC_2N_3S)_2$.

The most pronounced interaction is that between the two $3b_1$ orbitals (see Figure 4), which split apart to form the HOMO and LUMO of the dimer. While these orbitals retain much of their delocalized character (with respect to the individual rings), their overlap properties are such that they can be designated as bonding and antibonding with respect to the sulfur–sulfur contact. There are other orbitals (particularly the $1b_1$ and $2b_1$) further down the stack that also give rise to S–S bonding and antibonding combinations when the radical halves approach one another, but the net bonding effect from these interactions is small because both the bonding and antibonding combinations are occupied. The in-phase combination of the $3b_1$ orbitals of $H_2C_2N_3S$·, i.e., the HOMO of the dimer $(H_2C_2N_3S)_2$, is therefore the only bonding orbital whose counterpart is not filled. It is tempting to equate this orbital with what one would like to call a sulfur–sulfur σ bond, and, insofar as the local contributions from the two sulfur atoms are concerned, the orbital does have symmetry properties which are of a σ type. However, the orbital is considerably more diffuse than is the S(2p)–S(2p) σ orbital in, for example, H_2S_2. In a sense we are limited by the language of valence bond theory in which the term σ bond implies a two-electron two-center interaction. Clearly the S–S bond in **3** does not fall into such a category. Indeed the aps bond order[34] for the model dimer $(H_2C_2N_3S)_2$ is 0.26.

The above description of the dimer **3** has a direct parallel in the dithionite anion, which can be regarded as a pair of SO_2^-· radicals weakly coupled through their π* orbitals.[29] Like **3**, $S_2O_4^{2-}$

(34) Bond orders calculated as in: Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

readily dissociates in solution. In the present case the extent of the dissociation **3** ⇌ **2** has not been measured. However, as in the case of heterocycles such as $R_2C_2N_4S_2$, whose structures (i.e., **8** or **9**) can be predicted on the basis of the electron-releasing or -accepting properties of the exocyclic R groups,[22c,32] the equilibrium should be dependent on the nature of the groups attached to the carbon. Thus, dimerization should be favored by electron-donating substituents (e.g., *p*-NMe₂C₆H₄), which would destabilize the radical SOMO, and be suppressed by electron-withdrawing ones (e.g., *p*-NO₂C₆H₄).

Thus far we have not addressed directly the reason for the eclipsed conformation of the two C_2N_3S rings in **3**. Instead, because of the mutual inclination of the two rings, we have focused attention on the nature of the S–S interaction. However, the argument regarding this interaction could be developed for any orientation of the two rings (created by a torsion of one ring with respect to the other about the S–S vector). It is interesting to speculate whether **3** should be regarded as a π–π complex, in the sense usually reserved to describe the through-space interactions in cyclophanes.[35] In order to test this point we have carried out a series of MNDO calculations on $(H_2C_2N_3S)_2$ models by using different torsion angles about the S–S vector. However, no useful conclusion could be reached; the skewed orientation **10b** was found to be more stable than **10a** (by 6 kcal/mol) and **10c** (by 3 kcal/mol).

The present problem has a close analogy in the structures of the dimers **11** and **12**, which consist of pairs of 7π radicals linked through two long sulfur–sulfur interactions.[7,36] While one (**11**)


10a　　　**10b**　　　**10c**
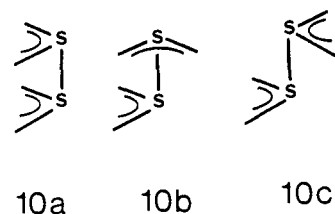
possesses a cis structure, the other (**12**) exhibits a trans arrangement of the two rings with respect to the S–S bridges. In

11　　　　　　　　**12**
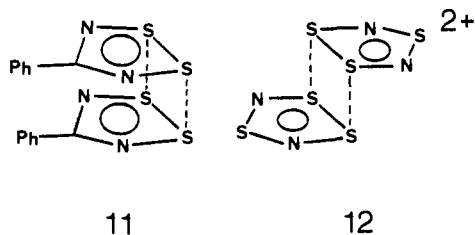
these latter examples and the present structure, the final geometry may well be determined by lattice or dispersion forces.[37] Clearly further synthetic, structural, and theoretical studies are required to clarify the issue.

Other Radicals Related to 2. The stability of the Ph₂C₂N₃S· radical provides a basis for considering the viability of other π radicals related to it. We draw attention to two examples of current interest. (1) The reduction of Ph₄P₂N₃SCl yields a 12-membered P₄N₆S₂ macrocycle.[38] ESR studies of this reaction[39] indicate the transient existence of a diphosphathiatriazinyl radical **13** as the initial reduction product (cf. **2**). Hyperfine coupling constants to the different nitrogens indicate that, consistent with

13　　　　　**14**
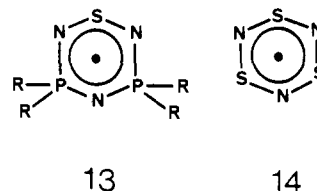
the expected electronegativity differences between P(V) and S(II), the SOMO is strongly polarized, with spin density localized over the NSN fragment. (2) The vaporization of the (SN)ₓ polymer leads to a molecular species which, upon condensation from the gas phase, reforms the polymer as epitaxial films.[1,40] Recent photoelectron and quadrupole mass spectrometric studies[41] of this gas-phase species have lead to the conclusion that it is the elusive S₃N₃· radical **14** (the "missing link" in binary SN chemistry). We are currently pursing ways of generating S₃N₃· in solution, e.g., by oxidation of S₃N₃⁻ or by reduction of S₃N₃Cl₃.[42] However, to date such experiments have yielded only S₄N₄ and traces of (SN)ₓ. We have been unable to observe (at room temperature) any ESR active species. Theoretical studies on a planar S₃N₃· radical suggests a 9π ²A₂ ground state;[41] while dimerization of the type observed for **2** therefore seems unlikely, the absence of any readily detectable signal suggests a rapid and irreversible association pathway for S₃N₃·.

Conclusions

1,2,4,5-Thiatriazinyl radicals can be prepared by the reduction of the corresponding 1-chloro substituted thiatriazine. These radicals exist in solution in equilibrium with a diamagnetic dimer. The crystal structure of bis(3,5-diphenyl-1,2,4,6-thiatriazine) (**3**) reveals a cofacial arrangement of the two C_2N_3S rings bridged by a long (2.666 (3) Å) sulfur–sulfur contact. Molecular orbital calculations on a $(H_2C_2N_3S)_2$ model reveal that, as in the case of the $S_2O_4^{2-}$ ion, the net bonding interaction between the two sulfur atoms arises from the overlap of the π* SOMO's of the radical partners, i.e., H₂C₂N₃S·. The length and weakness of the S–S interaction, which sets it apart from a regular disulfide bond, stems from the highly diffuse nature of the interacting orbitals. We conclude by noting that while the present system provides no indication of any ordering of dimer pairs into one dimensional arrays, e.g., **15**, it represents a useful test case for the design of

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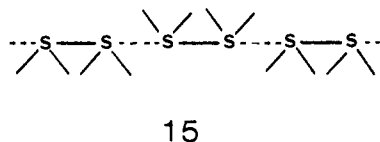
such systems. Modification of the 3,5-substituents of **3** may lead to subtle electronic and, hence, solid-state changes.

(35) (a) Doris, K. A.; Ellis, D. E.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2491. (b) Heilbronner, E.; Yang, Z-Z. *Top. Curr. Chem.* **1983**, *115*, 1 and references therein.

(36) (a) Gillespie, R. J.; Kent, J. D.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3784. (b) Small, R. W. H.; Banister, A. J.; Hauptman, Z. V. *J. Chem. Soc., Dalton Trans.* **1984**, 1377.

(37) The involvement of 3d orbitals has been suggested as the cause of the eclipsed conformation of S₂O₄²⁻ (see ref 29), but the argument is not compelling.

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