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1,2,4,6-Selenatriazinyl Radicals and Dimers. Preparation and Structural Characterization of 1-Chloro-3,5-diphenyl-1,2,4,6-selenatriazine ($Ph_2C_2N_3SeCl$) and Bis(3,5-diphenyl-1,2,4,6-selenatriazine) ($(Ph_2C_2N_3Se)_2$)

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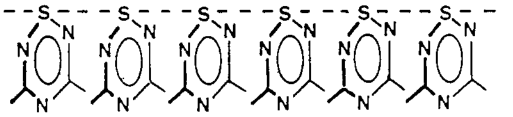
Abstract: 1-Chloro-3,5-diphenyl-1,2,4,6-selenatriazine ($Ph_2C_2N_3SeCl$) has been prepared by reaction of selenium tetrachloride with *N*-benzimidoylbenzamidine hydrochloride and pyrolysis (at 120 °C (0.01 Torr)) of the intermediate 1,1-dichloro-3,5-diphenyl-1,4-dihydroselenatriazine ($Ph_2C_2(NH)N_2SeCl_2$). Reduction of $Ph_2C_2N_3SeCl$ with triphenylantimony in methylene chloride generates the 3,5-diphenyl-1,2,4,6-selenatriazinyl radical $[Ph_2C_2N_3Se]^\bullet$ ($g = 2.017$, a_N (2 N) = 0.43 mT, a_N (1 N) = 0.38 mT). Like the corresponding 1,2,4,6-thiatriazinyl radical $[Ph_2C_2N_3S]^\bullet$, the selenatriazinyl radical $[Ph_2C_2N_3Se]^\bullet$ associates in solution to form a diamagnetic dimer; K_{diss} (in CH_2Cl_2 at 290 K) for $[Ph_2C_2N_3E]_2$ are 5 (±1) × 10^{-4} M and 3 (±1) × 10^{-2} M for E = Se and S, respectively. The crystal structures of $Ph_2C_2N_3SeCl$ and $[Ph_2C_2N_3Se]_2$ have been determined by X-ray crystallography. Crystals of the latter consist of cofacially aligned pairs of selenatriazinyl units with a *d*(Se- - -Se) distance of 2.792 (3) Å. Crystal data for $Ph_2C_2N_3SeCl$: orthorhombic; space group $P2_12_12_1$; $a = 6.999$ (3), $b = 10.826$ (2), $c = 18.004$ (3) Å; $V = 1364$ (1) Å^3; $Z = 4$ at 22 °C; $R = 0.054$ for 1083 reflections with $I > 3\sigma(I)$. Crystal data for $(Ph_2C_2N_3Se)_2$: triclinic; space group $P\bar{1}$; $a = 10.431$ (4), $b = 11.456$ (4), $c = 11.996$ (5) Å; $\alpha = 69.91$ (3), $\beta = 82.72$ (3), $\gamma = 88.57$ (3)°; $V = 1335$ (1) Å^3; $Z = 2$ at 22 °C; $R = 0.050$ for 1496 reflections with $I > 3\sigma(I)$.

Recently we described the preparation of the 3,5-diphenyl-1,2,4,6-thiatriazinyl radical TTA$^\bullet$ (**1**) and its association, in the solid state, into the cofacial dimer $(TTA)_2$ (**2**) (Scheme I).[2] This species represents one of a new and rapidly growing group of heterocyclic thiazyl radicals, which form dimeric units in the solid state linked through weak (long) interannular S- - -S interactions.[3–6] Encouraged by the stability of TTA$^\bullet$ to both oxidation (to TTA$^+$) and reduction (to TTA$^-$),[7] we are currently exploring the potential of radicals of this type as building blocks for the construction of low-dimensional metals.[8]

Although the packing arrangement for $(TTA)_2$ does not exhibit the desired ordered stacking **3**, we believe that such a pattern may well be achieved by modification of the exocyclic ligands or by substitution of the sulfur atom of TTA$^\bullet$ with one of its heavier congeners, e.g. selenium or tellerium.



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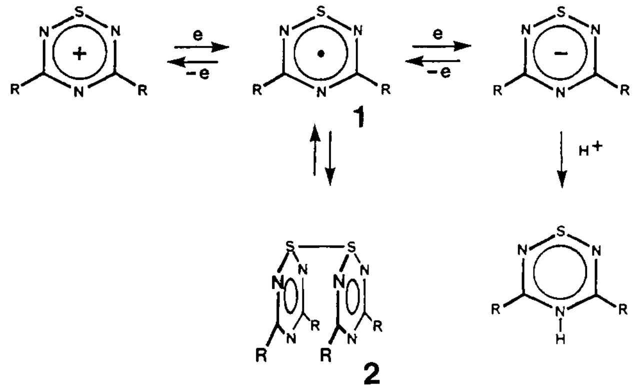
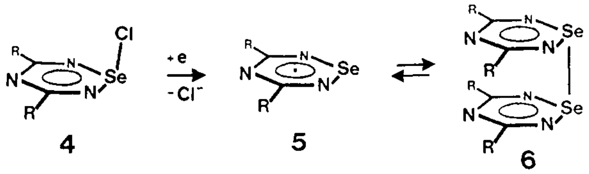
We have now designed a more flexible synthetic route to the TTA framework and have extended the method to afford the corresponding selenium ring system $Ph_2C_2N_3SeCl$ (**4**). Reduction of **4** with triphenylantimony produces the 1,2,4,6-selenatriazinyl radical SeTA$^\bullet$ (**5**), which, like its sulfur counterpart, forms a cofacial diamagnetic dimer $(SeTA)_2$ (**6**) in the solid state (eq 1). Herein we report the synthetic sequence to **4**, the ESR characterization of **5**, the thermodynamics of association of TTA$^\bullet$ and SeTA$^\bullet$, and the solid-state structures of **4** and **6**.

Scheme I





(1)

Experimental Section

Starting Materials and General Procedures. *N*-Benzimidoylbenzamidine hydrochloride was prepared as described by Peak[9] and dried at 110 °C (0.01 Torr) overnight prior to use. Elemental selenium (Aldrich) and chlorine gas (Matheson) were commercial products and were used as received. Sulfur dichloride (Aldrich) was redistilled from PCl_3 prior to use. The solvent acetonitrile was doubly distilled from P_2O_5 and CaH_2. Infrared spectra were recorded on Nujols mulls (with CsI cells) with a Nicolet 20DX/B FTIR spectrometer. Chemical analyses were performed by MHW laboratories, Phoenix, AZ. All melting points were measured on a Gallenkamp melting point apparatus and were uncorrected. EI mass

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

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Table I. Data for Structure Determinations

	A. Crystal Data	
formula	$C_{14}H_{10}N_3SeCl$	$C_{28}H_{20}N_6Se_2{\cdot}CH_3CN$
FW	334.7	639.5
F_{000}	664	640
no. of reflcns in cell detn	25	25
cryst syst	orthorhombic	triclinic
space gp; Z	$P2_12_12_1$; 4	$P\bar{1}$; 2
a, Å	6.999 (3)	10.431 (4)
b, Å	10.826 (2)	11.456 (4)
c, Å	18.004 (3)	11.996 (5)
α, deg		69.91 (3)
β, deg		82.72 (3)
γ, deg		88.57 (3)
V, Å^3	1364 (1)	1335 (1)
D_{calcd} g cm^{-3}	1.63	1.59
μ(Mo$K\alpha$), cm^{-1}	29.1	27.7
2θ range for cell detn, deg	20–24	8–22
total decay, %	<1	24.7
abs corrn	0.79–1.00	0.76–1.00
cryst size, mm	0.22 × 0.30 × 0.48	0.28 × 0.16 × 0.10
	B. Data Collection	
scan type	ω–2θ	ω–2θ
max (sin θ)/λ	0.70	0.55
no. of unique reflcns	2274	3492
no. of obsd data ($I > 3\sigma(I)$)	1083	1496
	C. Refinement	
H atom treatment	idealized	idealized
params refined	172	337
final R; R_w	0.054; 0.061	0.050; 0.058
max peak final diff map, e Å^{-3}	0.77 (8)	0.64 (8)
GOF	1.55	1.16

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.

Reaction of $[PhC(NH_2)NC(Ph)NH_2]Cl^-$ with SCl_2. An excess (ca. 0.5 mL) of sulfur dichloride was injected into a stirred slurry of N-benzimidoylbenzamidine hydrochloride (4.46 g, 17.2 mmol) in 150 mL of acetonitrile. A vigorous reaction ensued, liberating HCl gas and dissolving all the solid reagent to leave a yellow solution. After the solution was cooled to 0 °C, yellow transparent needles of $Ph_2C_2N_3SCl$ (4.15 g, 16.2 mmol, 94%) were formed. The product was collected by filtration under nitrogen, dried in vacuo, and identified by comparison of its IR spectrum with that of a known sample.[2]

Reaction of $[PhC(NH_2)NC(Ph)NH_2]^+Cl^-$ with $SeCl_4$. Dry chlorine gas was passed over a slurry of powdered selenium in 40 mL of CH_3CN (210 mg, 2.66 mmol) until all the selenium was transformed into white precipitate of selenium tetrachloride.[10] To this slurry was added N-benzimidoylbenzamidine hydrochloride (660 mg, 2.58 mmol). Both reagents rapidly dissolved to yield a yellow solution, which, upon cooling to 0 °C, yielded bright yellow needles of $[[PhC(NH_2)NC(Ph)NHCl]^+]_2[Se_2Cl_{10}]^{2-}$ (660 mg, 1.28 mmol), dec >100 °C. Anal. Calcd for $C_{28}H_{28}N_6Cl_{12}Se_2$: C, 32.59; H, 2.73; N, 8.14. Found: C, 32.71; H, 2.83; N, 8.32.

Preparation of $Ph_2C_2(NH)N_2SeCl_2$. Solid $[[PhC(NH_2)C(Ph)NHCl]^+]_2[Se_2Cl_{10}]^{2-}$ was heated at 60 °C (0.01 Torr) for 24 h. During this period, the yellow solid slowly decomposed to a white powder. This material was sparingly soluble in acetonitrile but could be crystallized in small quantities to produce small colorless needles of $Ph_2C_2(NH)N_2SeCl_2$, dec >160 °C. Anal. Calcd for $C_{14}H_{11}N_3Cl_2Se$: C, 45.27; H, 3.26; N, 11.31; Cl, 19.09. Found: C, 45.38; H, 3.36; N, 11.33; Cl, 18.88.

Preparation of $Ph_2C_2N_3SeCl$ (4). Solid $Ph_2C_2(NH)N_2SeCl_2$ was heated at 120 °C (0.01 Torr) for 48 h. During this period, the white powder slowly metamorphosed into small bright yellow crystalline nodules. This material was recrystallized from hot acetonitrile as pale yellow parallelepipeds of **4**, mp 185–187 °C. Typical yields for the overall conversion of selenium through both intermediates to **4** were approximately 60%. Anal. Calcd for $C_{12}H_{10}N_3SeCl$: C, 50.24; H, 3.01; N, 12.56; Cl, 10.59. Found: C, 50.21; H, 3.07; N, 12.52; Cl, 10.41. MS, m/e: 300 ($Ph_2C_2N_3Se^+$, 40%), 197 ($PhCN_2Se^+$, 11%), 103 ($PhCN^+$, 25%), 94 (SeN^+, 100%). IR (1600–250-cm^{-1} region): 1585 (w), 1330 (s), 1170 (m), 1125 (vw), 1060 (w), 1020 (m), 930 (w), 800 (w), 765 (w), 725 (s), 680 (s), 600 (m), 430 (m), 320 (m), 260 (m) cm^{-1}.

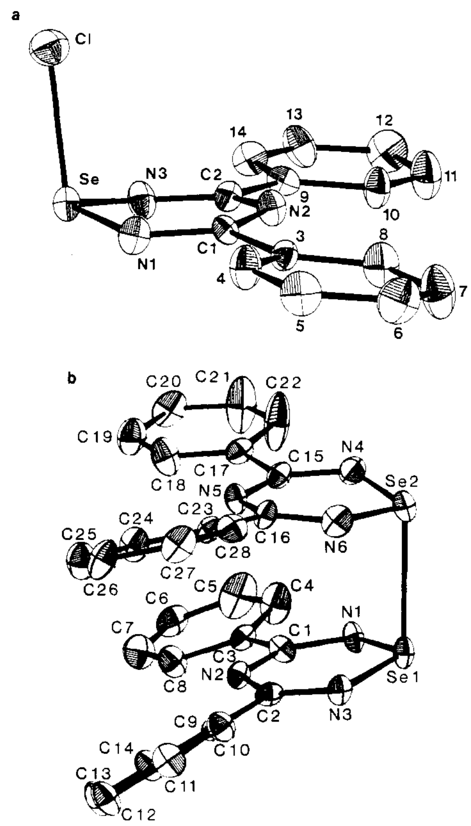

Figure 1. ORTEP drawings of (a) **4** and (b) **6**, showing atom-numbering schemes.

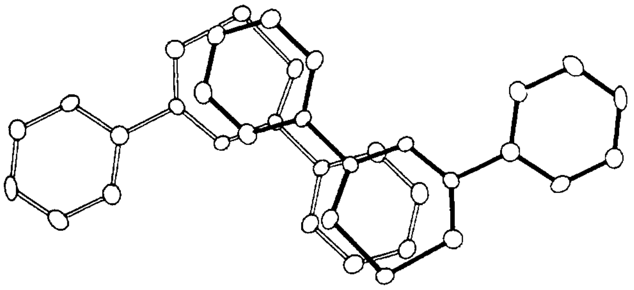

Figure 2. Illustration of phenyl-over-C_2N_3Se ring packing of $(Ph_2C_2N_3Se)_2$ dimer units in **6**.

Preparation of $(SeTA)_2$ (6). A solution of triphenylstibine (600 mg, 1.70 mmol) in 15 mL of acetonitrile was added to a stirred solution of **4** (569 mg, 1.70 mmol) in 20 mL of hot acetonitrile. The initially pale yellow solution turned deep red, and bright red crystals of $(SeTA)_2{\cdot}CH_3CN$ (370 mg, 1.24 mmol, 73%), dec >145 °C, rapidly formed. This material was then dried at 60 °C (0.01 Torr) for 24 h to remove the solvent of recrystallization. Anal. Calcd for $C_{28}H_{20}N_6Se_2$: C, 56.20; H, 3.37; N, 14.04. Found: C, 55.92; H, 3.50; N, 14.21. IR (1600–250 cm^{-1}): 1575 (b, m), 1430 (m), 1415 (m), 1320 (m), 1265 (m), 1230 (m), 1170 (m), 1140 (m), 1065 (w), 1050 (w), 1020 (s), 1000 (w), 930 (w), 850 (w), 820 (w), 790 (w), 725 (s), 680 (s), 640 (m), 610 (w), 600 (m), 410 (m), 370 (w), 320 (w) cm^{-1}.

X-ray Measurements on 4 and $6{\cdot}CH_3CN$. Crystals of **4** and $6{\cdot}CH_3CN$ were both grown from acetonitrile. In the case of $6{\cdot}CH_3CN$, the crystals were obtained directly from the reaction mixture. Data collection and refinement parameters are listed in Table I. Data collection procedures and computational methods were as previously described.[2,6] All nonhydrogen atoms in **4** were refined anisotropically, as were the non-hydrogen atoms of $(SeTA)_2$; those of the acetonitrile solvent molecule were refined isotropically. The relatively high σ's on the atom positions, bond distances, and bond angles in $6{\cdot}CH_3CN$ are attributed to poor crystal quality, the paucity of observed data, and crystal decomposition in the

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[10] Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic: New York, 1963; Vol. 1, p. 423.

Table II. Non-Hydrogen Atom Coordinates and B_{eq} Values

atom	x	y	z	B_{eq}, Å^2
		$Ph_2C_2N_3SeCl$		
Se	0.2083 (2)	0.2069 (1)	0.00945 (6)	2.58 (2)
Cl	0.3706 (6)	0.0979 (3)	−0.0841 (2)	4.46 (8)
N(1)	0.368 (1)	0.1853 (9)	0.0837 (5)	2.9 (2)
N(2)	0.197 (1)	0.0007 (9)	0.1216 (5)	2.9 (2)
N(3)	0.018 (1)	0.1052 (8)	0.0267 (5)	3.3 (2)
C(1)	0.337 (2)	0.0851 (9)	0.1254 (6)	2.5 (2)
C(2)	0.046 (2)	0.015 (1)	0.0748 (6)	2.5 (2)
C(3)	0.475 (2)	0.067 (1)	0.1864 (6)	2.4 (2)
C(4)	0.641 (2)	0.136 (1)	0.1898 (7)	3.8 (3)
C(5)	0.772 (2)	0.122 (1)	0.2464 (7)	3.8 (3)
C(6)	0.754 (2)	0.033 (1)	0.2983 (7)	5.1 (4)
C(7)	0.583 (2)	−0.036 (1)	0.2981 (8)	5.4 (4)
C(8)	0.453 (2)	−0.022 (1)	0.2406 (7)	4.2 (3)
C(9)	−0.103 (2)	−0.077 (1)	0.0797 (6)	2.7 (2)
C(10)	−0.104 (2)	−0.168 (1)	0.1363 (7)	3.8 (3)
C(11)	−0.247 (2)	−0.253 (1)	0.1413 (8)	5.4 (4)
C(12)	−0.387 (2)	−0.256 (1)	0.0896 (8)	5.5 (4)
C(13)	−0.396 (2)	−0.168 (1)	0.0349 (8)	4.5 (3)
C(14)	−0.252 (2)	−0.083 (1)	0.0303 (6)	3.7 (3)
		$(Ph_2C_2N_3Se)_2 \cdot CH_3CN$		
Se(1)	0.5218 (1)	0.4091 (1)	0.6726 (1)	3.06 (3)
Se(2)	0.3189 (1)	0.3041 (1)	0.6056 (1)	3.40 (3)
N(1)	0.4665 (9)	0.3653 (8)	0.8264 (8)	3.3 (2)
N(2)	0.3681 (8)	0.5663 (8)	0.7995 (7)	2.8 (2)
N(3)	0.4794 (8)	0.5683 (8)	0.6045 (7)	2.8 (2)
N(4)	0.2308 (9)	0.2457 (8)	0.7501 (8)	3.7 (3)
N(5)	0.1215 (8)	0.4415 (7)	0.7192 (7)	2.9 (2)
N(6)	0.2461 (9)	0.4506 (8)	0.5324 (8)	3.7 (3)
C(1)	0.398 (1)	0.4467 (9)	0.8651 (9)	2.9 (3)
C(2)	0.411 (1)	0.6166 (9)	0.6815 (9)	2.6 (3)
C(3)	0.355 (1)	0.408 (1)	0.9954 (9)	2.8 (3)
C(4)	0.363 (1)	0.286 (1)	1.069 (1)	5.7 (4)
C(5)	0.322 (1)	0.256 (1)	1.191 (1)	6.4 (4)
C(6)	0.279 (1)	0.341 (1)	1.241 (1)	4.5 (4)
C(7)	0.268 (1)	0.458 (1)	1.170 (1)	5.3 (4)
C(8)	0.306 (1)	0.494 (1)	1.047 (1)	4.1 (3)
C(9)	0.3776 (9)	0.7519 (9)	0.6282 (9)	0.2 (3)
C(10)	0.365 (1)	0.806 (1)	0.509 (1)	3.4 (3)
C(11)	0.337 (1)	0.930 (1)	0.459 (1)	3.9 (3)
C(12)	0.322 (1)	1.002 (1)	0.531 (1)	4.1 (3)
C(13)	0.331 (1)	0.949 (1)	0.650 (1)	4.4 (3)
C(14)	0.360 (1)	0.825 (1)	0.701 (1)	3.6 (3)
C(15)	0.152 (1)	0.326 (1)	0.7819 (9)	2.9 (3)
C(16)	0.162 (1)	0.492 (1)	0.602 (1)	2.9 (3)
C(17)	0.087 (1)	0.275 (1)	0.907 (1)	3.4 (3)
C(18)	0.010 (1)	0.345 (1)	0.959 (1)	4.8 (4)
C(19)	−0.047 (1)	0.299 (1)	1.077 (1)	5.2 (4)
C(20)	−0.031 (1)	0.181 (1)	1.142 (1)	5.0 (4)
C(21)	0.047 (2)	0.111 (1)	1.093 (1)	8.5 (5)
C(22)	0.101 (2)	0.154 (1)	0.978 (1)	8.4 (5)
C(23)	0.105 (1)	0.614 (1)	0.539 (1	2.7 (3)
C(24)	0.044 (1)	0.684 (1)	0.600 (1)	4.1 (3)
C(25)	−0.004 (1)	0.799 (1)	0.541 (1)	4.6 (4)
C(26)	0.004 (1)	0.841 (1)	0.420 (1)	4.3 (3)
C(27)	0.065 (1)	0.773 (1)	0.355 (1)	4.6 (4)
C(28)	0.113 (1)	0.659 (1)	0.415 (1)	3.6 (3)
C(29)	0.685 (2)	0.143 (2)	0.978 (2)	8.5 (5)[a]
C(30)	0.631 (2)	0.102 (2)	0.891 (2)	8.5 (5)[a]
N(7)	0.574 (2)	0.073 (2)	0.832 (1)	11.3 (5)[a]

[a] Isotropically refined values. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter B_{eq} defined as the following: $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B^{13} + bc(\cos\alpha)B_{23}]$.

Table III. Selected Bond Distance (Å) and Angle (deg) Data

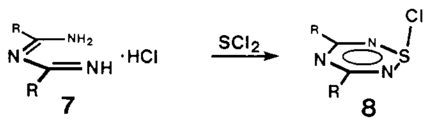
atom 1	atom 2	distance	atom 1	atom 2	atom 3	angle
			$Ph_2C_2N_3SeCl$			
Se	Cl	2.349 (3)	Cl	Se	N(1)	99.8 (3)
Se	N(1)	1.759 (7)	Cl	Se	N(3)	100.3 (3)
Se	N(3)	1.754 (8)	N(1)	Se	N(3)	105.4 (4)
N(1)	C(1)	1.337 (12)	Se	N(1)	C(1)	115.5 (7)
N(2)	C(1)	1.343 (12)	C(1)	N(2)	C(2)	121.4 (8)
N(2)	C(2)	1.358 (11)	Se	N(3)	C(2)	117.9 (7)
N(3)	C(2)	1.320 (11)	N(1)	C(1)	N(2)	130.0 (9)
			N(1)	C(1)	C(3)	114.6 (9)
			N(2)	C(1)	C(3)	115.3 (8)
			N(2)	C(2)	N(3)	127.1 (1)
			N(2)	C(2)	C(9)	116.5 (9)
			N(3)	C(2)	C(9)	116.2 (9)
			$(Ph_2C_2N_3Se)_2 \cdot CH_3CN$			
Se(1)	Se(2)	2.792 (3)	N(1)	Se(1)	N(3)	107.2 (4)
Se(1)	N(1)	1.761 (10)	N(4)	Se(2)	N(6)	105.2 (5)
Se(1)	N(3)	1.794 (9)	Se(1)	N(1)	C(1)	118.2 (8)
Se(2)	N(4)	1.769 (10)	C(1)	N(2)	C(2)	121 (1)
Se(2)	N(6)	1.805 (9)	Se(1)	N(3)	C(2)	113.7 (7)
N(1)	C(1)	1.33 (1)	Se(2)	N(4)	C(15)	115.9 (8)
N(2)	C(1)	1.38 (1)	C(15)	N(5)	C(16)	121 (1)
N(2)	C(2)	1.35 (1)	Se(2)	N(6)	C(16)	115.7 (8)
N(3)	C(2)	1.35 (1)	N(1)	C(1)	N(2)	127 (1)
N(4)	C(15)	1.34 (1)	N(2)	C(2)	N(3)	132 (1)
N(5)	C(15)	1.33 (1)				
N(5)	C(16)	1.34 (1)				
N(6)	C(16)	1.32 (1)				
C(1)	C(3)	1.48 (2)				
C(2)	C(9)	1.51 (1)				
C(15)	C(17)	1.49 (2)				
C(16)	C(23)	1.50 (2)				

X-ray beam. Non-hydrogen atom coordinates for both structures are provided in Table II, and pertinent bond distances and intervalence angles are summarized in Table III. ORTEP drawings of both **4** and **6**, giving the atom-numbering schemes, are shown in Figure 1, while Figure 2 illustrates the overlapping arrangement of neighboring dimer units in **6**·CH_3CN.

ESR Measurements on TTA• and SeTA•. ESR spectra and radical concentration measurements were performed on a Bruker ER 200D-SRC spectrometer with the ER-140 data system. The cavity temperature was maintained at 290 K by the Bruker ER 4111 VT variable-temperature unit. Intensity measurements were carried out with a series of oven-dried (150 °C) matched round cells cut from the same length of 4-mm-i.d. quartz tubing. Carefully weighed samples of each dimer ($(TTA)_2$ and $(SeTA)_2$) were transferred into the cells, and methylene chloride, dried by distillation from P_2O_5 and deoxygenated by storage over excess $(TTA)_2$, was then distilled into the cells on a vacuum line. The cells were then flame sealed, and the volume of solvent was determined by mass measurement.[11] The radical concentration in each cell was measured by comparison of the integrations of the second-derivative ESR spectra with a series of reference samples. The equilibrium constant (at 290 K) for each radical was calculated for the simple dissociation process; the reported values of K_{diss} for $(TTA)_2$ and $(SeTA)_2$ of 3 (±1) × 10^{-2} M and 5 (±1) × 10^{-4} M represent the averages taken from six measurements.

Results and Discussion

Preparation of $Ph_2C_2N_3SeCl$. *S*-Chlorothiatriazines have been prepared in a variety of ways. The reaction of sodium dicyanoamide with thionyl chloride affords $Cl_2C_2N_3SCl$,[12] while the reaction of benzamidine with $S_3N_3Cl_3$ provides direct access to $Ph_2C_2N_3SCl$.[2] Although this latter method provides a convenient source of small quantities of 3,5-diaryl-substituted compounds, it is both costly and limited in scope. We have therefore sought a more flexible and general route that would allow both modification of the exocyclic substituents and replacement of sulfur by selenium. In principle, the method of choice involves the condensation of an imidoylamidine with excess sulfur dichloride (eq 2). This approach has been successfully applied in the preparation of a variety of trichloromethyl-substituted (in 1- and/or 3-positions) derivatives[13] but has been limited by the paucity of known imidoylamidines.



(2)

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[11] Perkins, C. W.; Martin, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3211.

[12] Greevers, J.; Hackmann, J. Th.; Trompen, W. P. *J. Chem. Soc. C* **1970**, 875.

[13] Kornuta, P. P.; Derii, L. I.; Markovskii, L. N., *Zh. Org. Khim.* **1980**, *16*, 1303.

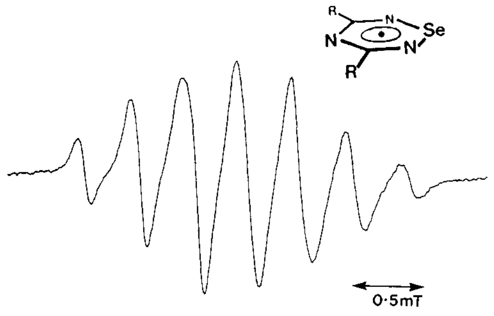
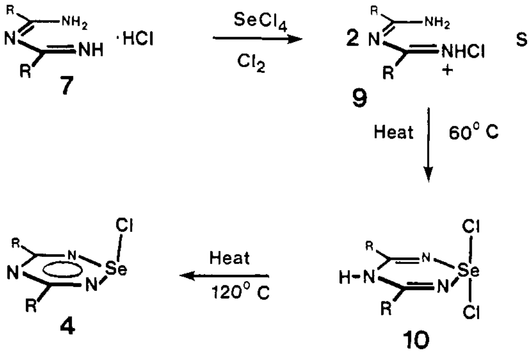


Figure 3. ESR spectrum of SeTA• in methylene chloride.

Scheme II



We have therefore examined the reported methods for generating these derivatives. In our hands, the base-promoted reaction of benzamidine with ethyl benzimidate has not led to the desired *N*-imidoylamidine **7** (R = Ph).[14] We have therefore resorted to the less direct but more reliable procedure of Peak,[9] which involves the treatment of *N*-thiobenzoylbenzamidine with benzamidine. The product **7**, isolated and used as its hydrochloride, reacts rapidly with excess sulfur dichloride to give $Ph_2C_2N_3SCl$ (**8**) in remarkably good (>90%) yield.

Extension of the above method to allow the incorporation of selenium was not a simple task. A number of steps, involving carefully controlled solid-state thermolyses, were required to reach the desired $Ph_2C_2N_3SeCl$. We chose to use selenium tetrachloride as a startiing reagent; this we were able to prepare quickly and easily in situ by the action of chlorine on a slurry of elemental selenium in acetonitrile. A pale yellow slurry of $SeCl_4$ generated in this way reacts directly with **7** (Scheme II) to produce the *N*-chloroimidoylamidinium decachlorodiselenate (**9**), whose composition and structure has been confirmed by both chemical and crystallographic analysis.[15] The reluctance of this material to eliminate HCl and condense to the desired product was not wholly unexpected and certainly reflects the known tendency of selenium(IV) to act as a strong acceptor to chloride ion. Elimination of HCl could be readily induced by heating **9** in the solid state at 60 °C (0.01 Torr), but the product so obtained, **10**, still contained an extra 1 mol equiv of hydrogen chloride and a four-coordinate selenium center (Scheme II).[16] The final elimination required that **10** be heated, again in the solid state, to 120 °C (0.01 Torr) for 48 h. Typical yields of $Ph_2C_2N_3SeCl$ (**4**), based on selenium, were approximately 60%.

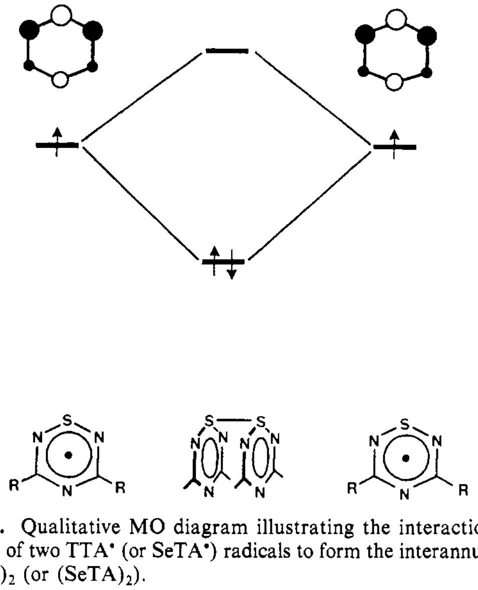


Figure 4. Qualitative MO diagram illustrating the interaction of the SOMO's of two TTA• (or SeTA•) radicals to form the interannular bond in $(TTA)_2$ (or $(SeTA)_2$).

Reduction of 4 and ESR Spectrum of SeTA• (5). Like the corresponding *S*-chlorothiatriazine $Ph_2C_2N_3SCl$, the *S*-chloroselenatriazine **4** can be easily reduced by triphenylantimony. When the reaction is carried out in deoxygenated methylene chloride, the resulting yellow solution exhibits an ESR signal (Figure 3) whose appearance is very similar to that of the corresponding thiatriazinyl radical TTA•. In TTA• the seven-line pattern is consistent with a delocalized radical in which hyperfine coupling to all three nitrogens is essentially equivalent (a_N = 0.397 mT). However, in SeTA• the lines are broadened relative to TTA•, and spectral simulation yields nonequivalent a_N values of 0.43 mT (2 N) and 0.38 mT (1 N). As in TTA•, there is no indication of "leakage" of spin density from the central C_2N_3Se ring onto the peripheral phenyl groups.

In our molecular orbital (MNDO) analysis of a model $H_2C_2N_3S^•$ radical, we found that the SOMO for the 7π-electron radical was the b_1 distribution shown in Figure 4. The essentially equivalent a_N values for all three nitrogen nuclei concur with this result. The slight redistribution of spin density in SeTA•, which parallels the differences observed between the radical anions of benzo-2,1,3-thiadiazole and benzo-2,1,3-selenodiazole,[17] suggests a slight polarization of the SOMO toward the N–Se–N nitrogens. It is more difficult to compare the spin densities at sulfur (in TTA•) and selenium (in SeTA•); although the *g* value in SeTA• (2.0169) is larger than in TTA• (2.0059), the increase may simply result from the presence of the heavier atom and its greater spin–orbit contribution to the *g* value.

Preparation and Crystal Structure of $(TSeA)_2$ (6). When the reduction of **4** is carried out in hot acetonitrile, bright red microcrystals of the diamagnetic dimer $(TSeA)_2$ (as its CH_3CN solvate) are precipitated from the solution in good yield (ca. 75%). Repeated efforts to grow single crystals suitable for X-ray work were eventually rewarded, although the size and shape of the crystals and their tendency to decompose in the X-ray beam led to a less than ideal ratio of observed reflections to parameters refined. The principal molecular and crystal structure features are nonetheless clear; as in **2**, crystals of **6**·CH_3CN consist of discrete cofacially bonded C_2N_3Se units whose mean planes make a dihedral angle of 11° (cf. 14° in **2**). The dimeric units do not assume a vertical stacking arrangement; instead, they pack in an alternating pattern, as illustrated in Figure 2, in which the phenyl group of one molecule overlaps the six-membered C_2N_3Se ring of its neighbor. The phenyl rings on each half of $(SeTA)_2$ are more twisted with respect to the C_2N_3Se plane (with dihedral angles ranging from 8 to 26°) than are those in $(TTA)_2$, but otherwise there are no substantive differences between the phenyl groups in $(TTA)_2$ and $(SeTA)_2$.

Just as the S- - -S separation in **2** (2.666 Å) is clearly longer than in a normal disulfide linkage, so to is the Se- - -Se contact in $(SeTA)_2$ (2.792 (3) Å) longer than a typical diselenide distance, e.g. in Se_8 (2.335 Å)[18] and similar to those found in the Se_4N_4 (2.75 Å)[19] and $Se_2I_4^{2+}$ (2.841 Å).[20] However, it is substantially

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(14) Oto, K.; Ichikawa, E. Japanese Patent 7303811 (Cl. C 07 cd), 1973.

(15) Privett, J. A. J.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W., submitted for publication in *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*

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shorter than the interannular Se- - -Se contacts observed in the dimer of the radical cation $SN_2Se_2^{\bullet+}$ (3.12–3.18 Å in its AsF_6^- and SbF_6^- salts).[21] A similar discrepancy has been noted[6] between the S- - -S contacts in **2** and those in $(S_3N_2)_2^{2+}$.[22,23] As in **2**, the interannular "bond" **6** can be visualized in terms of the overlap of the radical SOMO's (Figure 4) of the two halves, the two selenium 4p orbitals dominating the interaction.

Within the C_2N_3Se ring of **6**, the C–N and Se–N bonds show some minor deviations from those found in **4**, the most notable being the Se–N bonds, which are longer in $(SeTA)_2$ (mean 1.782 vs 1.757 Å in **4**). This lengthening may be interpreted as reflecting the occupation of the π^*-like orbitals on each ring whose in-phase combination (Figure 4) constitutes the net Se- - -Se "bond". Similar variations are observed between the S–N bonds in $Ph_2C_2N_3SCl$ and $(TTA)_2$.[2,7]

Thermodynamics of Association of TTA• and TSeA•. By double integrating the intensities of the ESR signals of solutions of TTA• and SeTA•, we have derived equilibrium constants for their association to $(TTA)_2$ on $(SeTA)_2$. Although we have not, as yet, been able to extend our work on $R_2C_2N_3E^\bullet$ radicals to include E = Te, the present data provide an initial basis for comparing the thermodynamics of association of $R_2C_2N_3E^\bullet$ as a function of the group VI element involved.

Dissociation of $(TTA)_2$ and $(SeTA)_2$ into their discrete radical components is only observed in solution; in the solid state at ambient temperatures, both dimers are diamagnetic. In methylene chloride the dissociation constant for $(TTA)_2$ ($K_{diss} = 3\ (\pm1) \times 10^{-2}$ M) is considerably greater than that found for aqueous dithionite $(S_2O_4)^{2-}$ ($K_{diss} = 1 \times 10^{-9}$ M),[24] suggesting that, solvation factors notwithstanding, the greater delocalization of spin density in TTA• weakens the interannular S- - -S "bond" in $(TTA)_2$ relative to that in dithionite. Comparable data have been obtained for the association of 1,2,3,5-dithiadiazolyls and $S_3N_2^{\bullet+}$.[25]

In $(SeTA)_2$ the dissociation constant decreases by 2 orders of magnitude to $5\ (\pm1) \times 10^{-4}$ M; i.e., the Se- - -Se bond is slightly stronger than the S- - -S bond in $(TTA)_2$. This observation is perhaps not that surprising, at least if one interprets the effect in terms of the greater spatial extension of selenium 4p orbitals compared to sulfur 3p orbitals.[26] If the concept is extended to the putative $Ph_2C_2N_3Te^\bullet$ radical TeTA•, strong interannular interaction should be attained at distances in excess of 3 Å. Whether such binding would remain localized, or whether some interdimer interactions could also be developed, remains to be seen. In this connection it appears important to design exocyclic ligands that will encourage a more uniform vertical arrangement of dimer units, e.g. **3**.

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Registry No. 1, 110874-98-1; **2**, 94405-47-7; **4**, 110874-99-2; **5**, 110875-00-8; **6**, 110875-01-9; **7**, 41908-69-4; **8**, 110875-02-0; $SeCl_4$, 10026-03-6; $[[PhC(NH_2)NC(Ph)NHCl]^+]_2[Se_2Cl_{10}]^{2-}$, 110875-04-2; $Ph_2C_2(NH)N_2SeCl_2$, 106483-94-7; $(SeTA)_2{\cdot}CH_3CN$, 110904-32-0; triphenylstibine, 603-36-1.

Supplementary Material Available: Anisotropic thermal parameters (Tables S1 and S2) (3 pages); listings of observed and calculated structure factors for structures **4** and **6**$\cdot CH_3CN$ (40 pages). Ordering information is given on any current masthead page.

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