

present. In contrast, cyclobutanylidene reacts primarily by ring contraction to give methylenecyclopropane along with smaller amounts of cyclobutene.¹³ This diverse behavior of the two carbenes is probably ascribable to the fact that rearrangement of **6a** to **7** is less exothermic than is rearrangement of cyclobutanylidene to methylenecyclopropane. Hortman and Bhatta-charjya did not find evidence for ring contraction of carbene **6b**.²

Acknowledgments. We are grateful to the National Science Foundation for support of this work under Grant CHE77-24624.

(12) Liberles, A.; Greenberg, A.; Lesk, A. *J. Am. Chem. Soc.* **1972**, *94*, 8685.

(13) Friedman, L.; Schechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.

Philip C. Martino, Philip B. Shevlin*

Department of Chemistry, Auburn University
Auburn, Alabama 36830

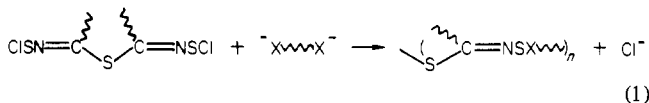
Received January 21, 1980

1,1-Dichloro-2,5-bis(*N*-chlorothioimino)-3,4-dicyano-selenophene

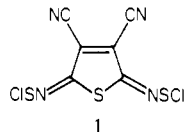
Sir:

Polymers with unsaturated sulfur (or selenium) and nitrogen and carbon backbones are of interest in regard to their potential electronic properties¹ because they are versatile extrapolations on the known inorganic superconducting polymer (SN)_x.

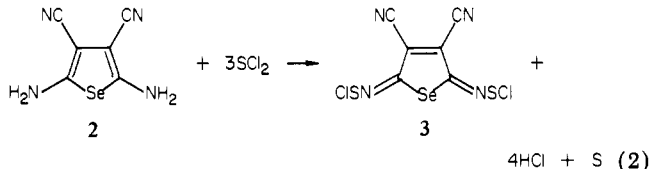
The SC=NSeCl moiety, while relatively unknown,³ could be used as an electrophile in condensation reactions as in eq 1.



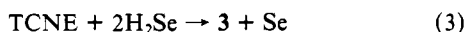
With this in mind, we designed the monomers **1**⁴ and **3**; it was expected that the latter could be prepared from the unknown



diamine **2** by a procedure developed for the preparation of **1**, namely, eq 2.



Reductive selenation of TCNE (eq 3) was expected to produce the diamine **2** in analogy with the synthesis of 2,5-diamino-3,4-dicyanothiophene.⁵



Here we report the preparation, characterization, and solid-state structure of the title compound produced in an attempted synthesis of **3** via reaction 2.

(1) F. Wudl, A. A. Kruger, and G. A. Thomas, *Ann. N.Y. Acad. Sci.*, **313**, 79 (1978).

(2) G. B. Street and W. D. Gill, *NATO Conf. Ser. [Ser.] 6*, **1**, 301-326 (1979), and references within.

(3) F. A. Davis, *Org. Prep. Proced. Int.*, **11**, 33 (1979); *Int. J. Sulfur Chem.*, **8**, 71 (1973).

(4) F. Wudl and E. T. Zellers, *J. Am. Chem. Soc.*, **102**, 4283 (1980).

(5) W. J. Middleton, V. A. Engelhardt, and B. S. Fisher, *J. Am. Chem. Soc.*, **80**, 2822 (1958).

Table I

Bond Distances (Å)			
Se1-Cl1	3.110 (1)	N1-C1	1.266 (4)
Se1-Cl2	2.369 (1)	N2-C3	1.138 (4)
Se1-C1	1.970 (3)	C1-C2	1.445 (4)
Cl1-S1	2.041 (1)	C2-C3	1.427 (4)
S1-N1	1.585 (3)	C2-C2	1.362 (6)
Bond Angles (Deg)			
Cl2-Se1-Cl2	173.46 (5)	S1-N1-C1	137.4 (3)
Cl2-Se1-C1	87.16 (9)	Se1-C1-N1	127.4 (2)
Cl2-Se1-C1	88.07 (9)	Se1-C1-C2	109.3 (2)
Cl2-Se1-C1	88.07 (9)	N1-C1-C2	123.3 (3)
Cl2-Se1-C1	87.16 (9)	S1-C2-C2	117.5 (2)
C1-Se1-C1	86.4 (2)	C1-C2-C3	120.3 (3)
Cl1-S1-N1	108.3 (1)	C2-C2-C3	122.2 (2)
		N2-C3-C2	179.2 (4)

^a Numbers in parentheses are estimated standard deviations in the least-significant digits.

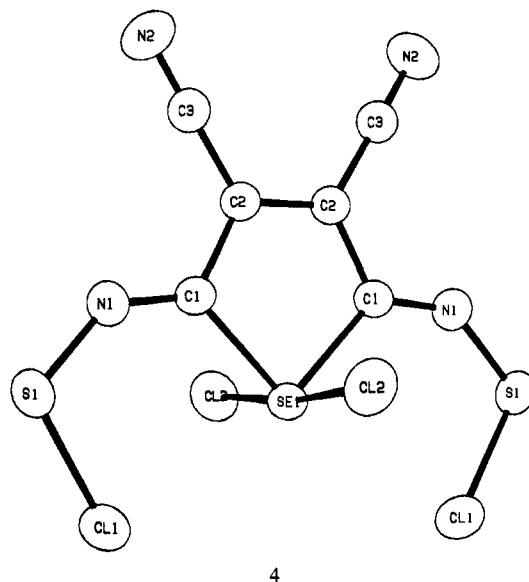


Figure 1. Molecular structure of 1,1-dichloro-2,5-bis(chlorothioimino)-3,4-dicyanoselenophene.

Reaction 3 did indeed produce the diaminoselenophene **2** in good yield as a salmon-colored solid⁶ which was insoluble in most organic solvents and exhibited chemical properties similar to those of its sulfur analogue.⁷ On the other hand, when **2** was exposed to sulfur dichloride under conditions identical with the preparation of **1**, compound **4** was produced instead of **3**. Since sulfur chlorides are known to disproportionate readily,⁸ it was not surprising (after the fact) to isolate **4** instead of **3** because selenium is more electropositive than sulfur and can expand its valence octet more readily than sulfur⁸ (cf. **1** which is devoid of chlorines in the 1-position).

Thus, **4** was produced in good yield as black prisms,⁹ whose structure could not be determined solely on the basis of its spectral properties: IR (KBr) 2225 (vw), 1520 (m), 1490 (s), 1330 (s), 1227 (w), 849 (m), 812 (s) cm⁻¹; mass spectrum (MS), *m/e* 344 (P + 2), 342 (P), 307 (P - Cl), 272 (P - Cl₂), etc. Note that the elemental analysis was low on Cl for **4** and high for **3** and the MS was correct for **3**; furthermore, the IR spectra of **4** and **1** were practically identical which led us to believe that the product from reaction 2 was indeed **3**.¹⁰ It was clear that in order to elucidate

(6) Anal. Calcd for C₆H₄N₄Se: C, 34.12; H, 1.90; N, 26.54; Se, 37.44. Found: C, 34.07; H, 2.22; N, 25.87; Se, 37.64.

(7) F. Wudl, E. T. Zellers, and D. Nalewajek, *J. Org. Chem.*, in press.

(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley-Interscience, New York, 1972, p 421 ff.

(9) Anal. Calcd for C₆Cl₂N₄S₂Se: C, 21.05; Cl, 20.76; N, 16.37; S, 18.70; Se, 23.09. Found: C, 19.22; Cl, 28.11; N, 15.11; S, 15.26; Se, 22.03. Calcd for C₆Cl₄N₄S₂Se: C, 17.43; Cl, 34.38; N, 13.56; S, 15.49; Se, 19.12.

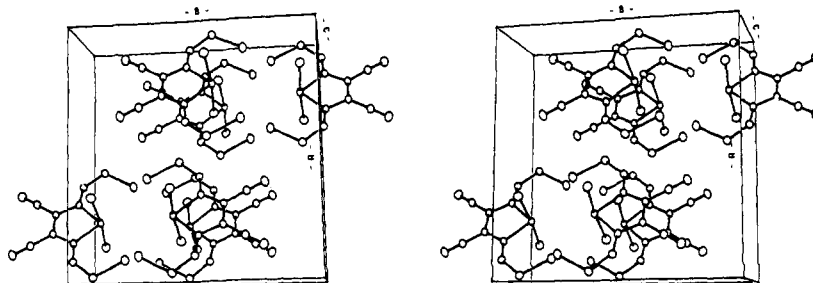


Figure 2. Stereoview of solid-state structure of molecules depicted in Figure 1.

Table II. Intermolecular Contacts to 3.8 Å^a

Cl1-Cl1	3.706 (5)	N2-C2	3.475 (5)
Cl1-Cl2	3.305 (1)	N2-C2	3.363 (5)
Cl2-Cl2	3.770 (6)	N2-C3	3.491 (5)
Cl1-N	3.351 (3)	N2-C3	3.207 (5)
Cl2-S1	3.360 (1)	C3-C3	3.438 (7)
S1-N2	3.119 (3)		

^a Numbers in parentheses are estimated standard deviations in the least-significant digits.

the structure with certainty, we had to resort to X-ray crystallography.¹¹

A 0.1 × 0.2 × 0.2 mm crystal mounted in a sealed capillary tube was employed for data collection. This was necessary since the solid loses chlorine slowly on standing. The space group and cell data are as follows:¹¹ system, monoclinic; centering, I-centered; space group, *I2/a*; extinctions, *hkl* (*h* + *k* + *l* ≠ 2*n*) *h0l* (*h* ≠ 2*n*, *l* ≠ 2*n*); cell constants, *a* = 14.206 (6), *b* = 13.737 (3), *c* = 6.882 (4) Å; α = 90, β = 91.60 (5), γ = 90°; *V* = 1342.5 Å³; λ = 0.710730 Å; calculated density, 2.043 g/cm³; molecules per unit cell, 4; linear absorption coefficient, 40.70 cm⁻¹; *F*(000), 792.

Intramolecular bond distances and angles are listed in Table I. Intermolecular contacts are listed in Table II. Figures 1 and 2 display the molecular and solid-state structures, respectively.

As in the case of **1**,⁴ the S-Cl bonds are directed inward toward the heterocycle's chalcogen atom; however, in the case of **4**, the Se-Cl1 distance is even shorter (3.110 vs. 3.29 Å in **1**), i.e., 0.54 Å shorter than the sum of van der Waals radii¹³ of Se and Cl. Neither the Se-Cl2 distances (2.24–2.38 Å) nor the Se-C distances (or the C-Se-C angle) are unusual.¹⁴ On the other hand,

the pseudooctahedral coordination¹⁵ around Se and the Cl2-Se-Cl2 angle are unusual. It is possible that these chlorines are bent toward the ring because of electron-electron repulsion between the remaining lone pair on selenium and the nonbonded electrons on the chlorines or¹⁶ because of electrostatic attraction between these chlorines and the electron-deficient carbons (C2, Figure 1).

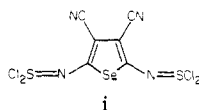
In the crystal packing structure, there are several unusual features. The molecules form stacks along *c* and sheets within the *a-b* plane. Whereas **1** forms head-to-tail sheets, **4** forms chlorine "clusters" by head-to-head ordering. As depicted in Figure 2, very short intermolecular Cl-Cl contacts are thus generated. For example, the intermolecular Cl1-Cl2 contact of 3.305 Å is 0.20 Å shorter than the sum of Cl van der Waals radii. This could explain the slow solid-state loss of chlorine at room temperature with the concomitant poor agreement in elemental analyses⁹ and the M-Cl₂ molecular ion peak in the mass spectrum.

In the solid state, apart from the loss of chlorine, the compound is stable to the atmosphere and can be kept in a plastic-capped vial at ambient temperature for months.¹⁷ Since the title molecule is rather electron deficient, it can be expected to be a powerful electrophile and oxidizing agent. Reactions with nucleophiles⁷ (substitution, condensation, polymerization) and mild reducing agents⁷ are currently under active investigation,^{7,18} and will be the subject of publications elsewhere⁷ and in the future.

Acknowledgments. We thank Professor F. A. Davis, Drexel University, for reprints and preprints in the field of sulfenimines and sulfenamides.

Supplementary Material Available: Positional and thermal parameters and thermal factors for **4** (1 page). Ordering information is given on any current masthead page.

(10) Another possible structure which was not ruled out from the available data was **i**.



(11) Molecular Structure Corp. College Station, TX 77840.

(12) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.041$. $R_2 = [\sum_w (|F_o| - |F_c|)^2 / \sum_w F_o^2]^{1/2} = 0.047$. Additional data available on request.

(13) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(14) I. L. Karle and J. Karle in "Organic Selenium Compounds", D. L. Klayman and W. H. H. Günther, Eds., Wiley, New York, 1973, pp 989–1015.

(15) For recent discovery of octahedral coordination around an electron-deficient sulfurane, see: L. D. Martin, E. F. Perozzi, and J. C. Martin, *J. Am. Chem. Soc.*, **101**, 3595 (1979).

(16) Professor E. M. Burgers has suggested this explanation on the basis of recent calculations; private communication.

(17) The plastic cap turns yellow after ca. 1 day at room temperature (Cl₂ evolution), but the crystals do not change in appearance by microscopic examination.

(18) E. T. Zellers, unpublished results.

F. Wudl,* E. T. Zellers

Bell Laboratories

Murray Hill, New Jersey 07974

Received March 3, 1980