(5) All new compounds reported in this work gave satisfactory spectral and analytical analyses.
(6) Woodward, R. B.; Pachter, I. J.; Scheinbaum, M. L. *Org. Synth.* **1974,** *54,* 33, 39.
(7) Cf. Marshall, J. A.; Seitz, D. E. *J. Org. Chem.* **1974,** *39,* 1814.
(8) Cf. Ishizumi, K.; Koga, K.; Yamada, S. *Chem. Pharm. Bull.* **1968,** *16,* 492.
(9) Takano, S.; Hatakeyama, S.; Ogasawara, K. *J. Am. Chem. Soc.* **1976,** *98,* 3022; **1979,** *101,* 6414.
(10) Heating at reflux temperature shortened the reaction time but led to predominant formation of an undesired isomer of the cyclization product.
(11) Crabb, P. A.; Newton, R. F.; Jackson, D. *Chem. Rev.* **1971,** *71,* 107.
(12) Uskokovic, M.; Bruderer, H.; von Planta, C.; Williams, T.; Brossi, A. *J. Am. Chem. Soc.* **1964,** *86,* 3364.
(13) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976,** *41,* 1485.
(14) We are greatly indebted to Professor J. Ficini (Université Pierre et Marie Curie, Paris), Professors H.-P. Husson and P. Potier (Institute de Chimie des Substances Naturelles, Gif/Yvette), and Professor J. A. Lamberton (CSIRO Chemical Research Laboratories, Melbourne) for generously providing a sample of natural antirhine.
(15) (a) Brown, H. C.; Ayyangar, N. R.; Zweifel, G. *J. Am. Chem. Soc.* **1964,** *86,* 397. (b) Hill, R. K.; Edwards, A. G. *Tetrahedron* **1965,** *21,* 1501. (c) McDonald, R. N.; Steppel, R. N. *J. Am. Chem. Soc.* **1969,** *91,* 782. (d) Takano, S.; Iwata, H.; Ogasawara, K. *Heterocycles* **1978,** *9,* 845.

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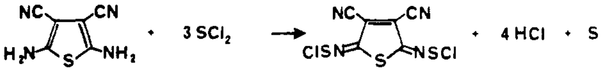
Received December 20, 1979

2,5-Di-*N*-chlorothioimino-3,4-dicyanothiophene: A Novel Monomer of Unusual Molecular and Solid-State Structure

Sir:

The title compound (**1**) was a molecule we sought as a possible monomer for the preparation of polymers of unsaturated sulfur-nitrogen-carbon backbone.[1] These polymers are of interest because they are expected to exhibit high electronic conductivity in the solid state in analogy[2] to $(SN)_x$. Here we describe the preparation and some properties of this heterocycle and its unique solid-state structure.

The *S*-chlorosulfurimino functional group is rare[3,4] and was isolated only in the case of highly electronegatively substituted small molecules.[5] It was, therefore, uncertain whether the title compound could be prepared and isolated for complete characterization. Fortunately, the mild conditions shown in eq[6] 1



(1)

1

afforded **1** in good yield as red crystals: IR (KBr) 2230 (vw), 1530 (s), 1500 (s), 1345 (s), 1240 (w), 892 (s), 841 (s), 820 (m) cm^{-1}; MS (*m/e*) 296 (P + 2), 294 (P), 259 (P − Cl), 224 (P − Cl_2), 192 (P − SCl_2), 146 (P − $NSCl_2$), etc. Anal. Calcd for $C_6Cl_2N_2S_3$: C, 24.41; Cl, 24.07; N, 18.98; S, 32.54. Found: C, 24.21; Cl, 23.93; N, 18.66; S, 32.83. Since attempts to determine its ^{13}C NMR spectrum failed owing to low solubility in most appropriate solvents and molecular weight determinations in solution again failed because of the instability of the compound in suitable solvents, we had to resort to X-ray structure determination.[7]

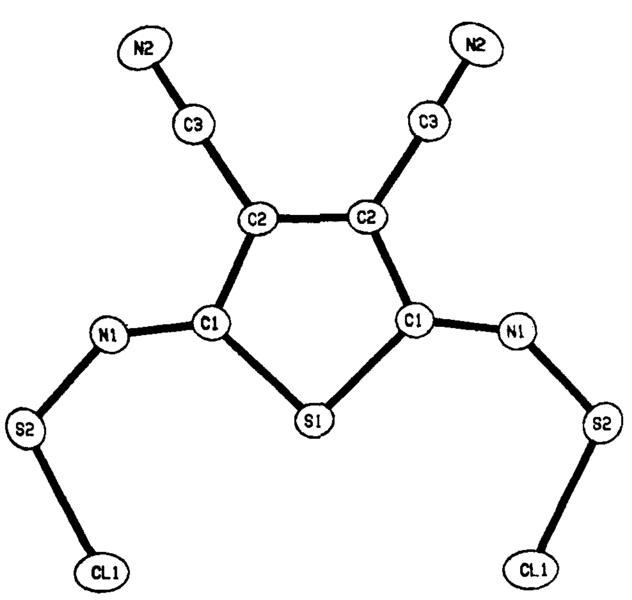


Figure 1. Molecular structure of 2,5-di-*N*-chlorothioimino-3,4-dicyanothiophene.

Data were collected on a 0.2 × 0.2 × 0.2 mm crystal mounted on a glass fiber. The orthorhombic *C*-centered (space group *Cmcm*) solid with extinctions *hkl* ($h + k \neq 2n$); *h0l* ($h = 2n$, $l \neq 2n$) had the following cell constants: $a = 6.327$ (3), $b = 9.678$ (8), $c = 17.337$ (17) Å; $\alpha = \beta = \gamma = 90°$; $V = 1061.7$ Å^3; $\lambda = 0.710730$ Å (based on computer centering of 25 reflections followed by least-squares refinement of the setting angles). Calculated density was 1.847 g/cm^3 for four molecules per unit cell of above dimensions.[8]

Intramolecular bond angles and bond distances are shown in Table I; molecular and solid-state structures are shown in Figures 1 and 2. The most striking features of the molecular structure are planarity and the inward folding of the S-Cl bonds such that the S-1 to Cl-1 distance (cf. Table I and Figure 1) of 3.29 Å is 0.26 Å shorter than the sum of Van der Waals radii for S and Cl.[9]

The solid-state structure reveals uniform stacks along the *a* axis and sheets along the *b*-*c* plane. The closest intermolecular contact (3.110 Å) is between Cl-1 and N-2 of two molecules within a sheet in the *b* direction (cf. Figure 2).

Although compound **1** could be considered an acid chloride

Table I[a]

Bond Distances in Ångstroms

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
S-1	Cl-1	3.290 (1)	N-1	C-1	1.283 (2)	C-2	C-2	1.363 (3)
S-1	C-1	1.775 (1)	N-2	C-3	1.136 (2)			
S-2	Cl-1	2.049 (1)	C-1	C-2	1.439 (2)			
S-2	N-1	1.583 (1)	C-2	C-3	1.431 (2)			

Bond Angles in Degrees

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C-1	S-1	C-1	91.3 (1)	S-1	C-1	C-2	110.2 (1)	C-2	C-2	C-3	123.39 (9)
Cl-1	S-2	N-1	111.29	N-1	C-1	C-2	120.8 (1)	N-2	C-3	C-2	178.5 (2)
S-2	N-1	C-1	138.5 (1)	C-1	C-2	C-2	114.13 (8)				
S-1	C-1	N-1	129.0 (1)	C-1	C-2	C-3	122.5 (1)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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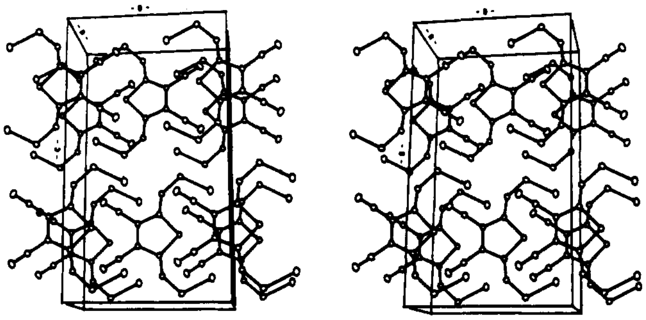

Figure 2. Stereoview of solid-state structure of molecules depicted in Figure 1.

(sulfenyl chloride), it is stable to the atmosphere in the solid state and can be recrystallized from chlorinated solvents but is unstable in solution in polar (e.g., acetonitrile) or Lewis basic (e.g., THF) solvents. Nucleophiles and reducing agents attack this molecule readily.[10] Reaction paths are complicated; for example, treatment with excess tetrabutylammonium iodide in homogeneous solution affords a conducting (260 Ωcm compaction), black, amorphous solid of empirical formula

$$C_{38}H_{36}N_{18}S_9{=}[(C_{22}N_{17}S_9)^- \cdot (C_4H_9)_4N^+]_n{}^{11}$$

The $(C_4H_9)_4N^+$ ion can be exchanged completely by $TTF^{+\cdot}[TTF_3(BF_4)_2]$ in benzonitrile to produce a solid $[(C_{18}H_4N_8S_8)_n]$ which exhibits a compaction conductivity[10,11] of 19 Ω cm.

The physical, chemical, and solid-state properties of materials derived via condensation and reduction reactions of the title compound are being actively pursued[10] and will be described elsewhere and in future publications.

Acknowledgment. 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 temperature factors for **1** (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) F. Wudl, A. A. Kruger, and G. A. Thomas, *Ann. N.Y. Acad. Sci.*, **313,** 79 (1978).
(2) G. B. Street, S. Etemad, R. H. Geiss, W. D. Gill, R. L. Greene, J. Kuyper, and R. D. Smith, *Ann. N.Y. Acad. Sci.*, **313,** 737 (1978), and references therein.
(3) F. A. Davis, *Org. Prep. Proced. Int.*, **11,** 33 (1979).
(4) F. A. Davis, *Int. J. Sulfur Chem.*, **8,** 71 (1973).
(5) J. Geevers and W. P. Trompen, *Tetrahedron Lett.*, 1687 (1974).
(6) Diaminodicyanothiophene was prepared according to the procedure given in W. J. Middleton, V. A. Engelhardt, and B. S. Fisher, *J. Am. Chem. Soc.*, **80,** 2822 (1958).
(7) Complete structure analysis by Molecular Structure Corporation, College Station, Texas 77840.
(8) Additional crystallographic data are given below. Diffraction; Enraf-NoniusCAD4. Mo Kα radiation filtered by a graphite crystal incident beam monochromator: temperature, 23 ± 1 °C; number of independent reflections, 1354; total number of reflections collected, 1402. Least-squares refinement: $R_1 = \Sigma\|\,|F_o| - |F_c|\|/\Sigma|F_o| = 0.029$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2} = 0.042$.
(9) A Bondi, *J. Phys. Chem.*, **68,** 441 (1964).
(10) F. Wudl, E. T. Zellers, and D. Nalewajek, submitted for publication; E. T. Zellers, unpublished results.
(11) The solid-state ESR spectra of the $(C_4H_9)_4N^+$ and $TTF^{+\cdot}$ salts had *g* values of 2.0025 and 2.0071, respectively.[10]

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Received February 8, 1980

Book Reviews

Kirk-Othmer Encyclopedia of Chemical Technology. Volume 6. Edited by M. GRAYSON. Wiley/Interscience, New York. 1979. xxiii + 869 pp. $120.00.

From Chocolate and Cocoa to Coffee, from Chromium to Copper, from Contact Lenses to Contraceptive Drugs, with diversions to Coal, Color, and Computers, this is a fascinating volume. As usual for the series, the articles include some historical background, some economics, a quantity of chemistry that varies according to the subject, and many tables and illustrations. There are 34 entries, which thus average over 20 pages each, contributed by experts drawn largely from American industries. The editing has been thorough, such that the treatment of such pervasive subjects as physical units, chemical nomenclature, structural formulas, etc., is consistent throughout. The quality of both production and content is high.

Aldehydes—Photometric Analysis. Volume 5. Formaldehyde Precursors. By EUGENE SAWICKI and CAROLE R. SAWICKI. Academic Press, London and New York. 1978. xi + 408 pp. £22.00.

A great variety of compounds can give rise to formaldehyde under environmental or biological conditions or in the laboratory. The reactivity of the formaldehyde provides a means for analysis, utilizing one of the several color-forming reactions with such reagents as chromotropic acid (naphthalene-1,8-diol-3,6-disulfonic acid). Terminal olefins, all varieties of *N*-methyl compounds, methyl sulfoxides, etc., are amenable to this sort of determination. This book is a thorough treatment of the subject, covering both established analytical methods and reactions with analytical potential. For each type of substance, a wealth of ancillary information is given, with emphasis on environmental and biological occurrence and significance. Experimental procedures are described, and the reactions involved are elucidated by structural equations. Access to desired information is provided by a detailed index, plus an extensive table of precursor substances with the reagent used to generate formaldehyde from them, and references. The bibliography contains 1537 references.

Advances in Heterocyclic Chemistry. Volume 24. Edited by A. R. KATRITZKY and A. J. BOULTON. Academic Press, New York. 1979. xi + 461 pp. $48.00.

Advancing knowledge has made out of date so many areas of heterocyclic chemistry that were adequately reviewed ten to fifteen years ago, that a major effort is warranted to bring the subjects abreast of current understanding. In this volume, no less than seven subjects of earlier chapters have been brought up to date: Quinazolines (W.J.F. Armaregs); Three-membered Rings with Two Heteroatoms (E. Schmitz); Physicochemical Aspects of Purines (J.H. Lister); Reissert Compounds (F.D. Popp); Pyridazines (M. Tišler and B. Stanovnik); Selenium-Nitrogen Heterocycles (I. Lalezari, A. Shafiee, and M. Yalpani); and Pyrrolizindines (D.J. Robins). There are two chapters on new subjects: Benzo[*c*]cinnolines (J.W. Barton), and 1,4-Thiazines (R.J. Stoodley).

Certain of the contributors have been careful to state the period over which they have reviewed the literature (e.g., "through 1976", "to the middle of 1976", etc.), but others have unfortunately made no mention of this important matter, and one has written "the past 25 years", without stating the year of termination, and another has written the vague description "during or after 1979". One misses a subject index in a work such as this, although it must be conceded that it would have to be fairly large. There is the usual cumulative index of titles of chapters beginning with Volume 1, however. The quality of this volume maintains the high standard of the series, and it continues to be an invaluable reference; the number of references in a chapter approaches 1000 in some cases, and the patent literature has not been neglected.

Organic Electronic Spectral Data. Volume XV. 1973. Edited by J. P. PHILLIPS, D. BATES, H. FEVER, and B. S. THYAGARAJAN. Wiley/Interscience, New York. 1979. xiii + 1194 pp. $55.00.

This series continues vigorously, collecting the enormous amount of new data on the visible and ultraviolet spectra of organic substances. A team of contributors have made the bibliographic searches, and the information has been processed at the University of Louisville to

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* Unsigned book reviews are by the Book Review Editor.