the optimum yields obtainable since a complete study of reaction variables was not made. One might, however, expect to get better yields using a larger excess of N_2F_4.

A reasonable mechanism for the reaction of N_2F_4 with RSF_5 and R_2SF_4 which accounts for the observed products and stoichiometry involves initial thermal cleavage of the sulfur compound to yield radicals and SF_4.

$$R \mid SF_4 \mid F \longrightarrow R\cdot + SF_4 + F\cdot$$
$$R \mid SF_4 \mid R \longrightarrow 2R\cdot + SF_4$$

Recombination of these radicals with $\cdot NF_2$ (from thermal equilibrium with N_2F_4) and with each other yield the observed products. Where NF_3 is used as the source of $\cdot NF_2$ groups, a step in which a fluorine abstraction from NF_3 by R· seem likely

$$R\cdot + NF_3 \longrightarrow RF + \cdot NF_2$$

This would account for the lower yields of RNF_2 (based on the sulfur compound) and larger amounts of RF observed.

It might be mentioned that attempts were made to extend this reaction to the preparation of hydrocarbon difluoroamine compounds but without success. The compound CH_3NF_2 has been reported by Frazer[14] as resulting from ultraviolet-initiated reaction of CH_3I with N_2F_4. Since the mechanism of this reaction undoubtedly involves a methyl free radical, it seemed likely that CH_3SF_5 might pyrolyze in an atmosphere of $\cdot NF_2$ radicals to give $CH_3\cdot$ and by radical combination yield CH_3NF_2. This compound might not be stable enough, however, to survive the temperatures necessary to thermally crack the CH_3SF_5. One might therefore expect to get either little or no CH_3NF_2: but one might reasonably expect to get HCN which is its dehydrohalogenated product. The failure to obtain evidence of CH_3NF_2 formation would suggest that CH_3SF_5 does not yield methyl radical on cracking. The CH_3F which results from pyrolysis of CH_3SF_5 could possibly form *via* an intramolecular attack of an adjacent fluorine atom. Like CH_3SF_5, the phenyl derivative $C_6H_5SF_5$ underwent thermal cracking in the presence of N_2F_4 to yield only fluorobenzenes with no evidence of formation of $C_6H_5NF_2$.

This work was done under the auspices of the U.S. Atomic Energy Commission. The authors wish to thank James A. Happe of the Lawrence Radiation Laboratory for his help in n.m.r. spectroscopy.

[14] J. W. Frazer, *J. Inorg. Nucl. Chem.*, **11**, 166 (1959).

[CONTRIBUTION NO. 755 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Thiacyanocarbons. I. Tetracyano-1,4-dithiin, Tetracyanothiophene and Tricyano-1,4-dithiino[c]isothiazole[1]

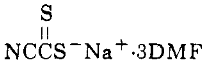
BY HOWARD E. SIMMONS, ROBERT D. VEST, DALE C. BLOMSTROM, JOHN R. ROLAND AND THEODORE L. CAIRNS

RECEIVED MARCH 24, 1962

Disodium dimercaptomaleonitrile has been found to be a versatile intermediate for the synthesis of thiacyanocarbons, molecules which contain only carbon, nitrogen and sulfur and a plurality of cyano groups. Oxidation of this salt has given tetracyano-1,4-dithiin, which can be further converted to tetracyanothiophene by heat. Reaction of tetracyano-1,4-dithiin with sulfur in the presence of nucleophiles gave tricyano-1,4-dithiino[c]isothiazole by a novel insertion mechanism. The physical and chemical properties of these compounds are reported preliminarily.

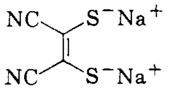
Introduction

Recently, Bähr and Schleitzer[2] have described the reaction of sodium cyanide and carbon disulfide in dimethylformamide to give a crystalline solvate of sodium cyanodithioformate **1** and further the unusually facile dimerization of **1** with loss of sulfur to form disodium dimercaptomaleonitrile(**2**).



$$NC\overset{\overset{S}{\|}}{C}S^-Na^+\cdot 3DMF$$

1



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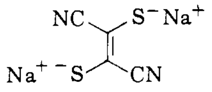

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We have studied the chemistry of salts **1** and **2**, and this series of papers[3] presents some of our results. The successful synthesis of disodium dimercaptofumaronitrile (**3**)[2a] has allowed a study of the stereochemistry and stability of the isomers **2** and **3**. In papers III[3b] and IV[3c] the mechanism of the oxidation of salts **1**, **2** and **3** to give tetracyano-1,4-dithiin (**4**) is presented in detail.

The present paper describes the synthesis and properties of tetracyano-1,4-dithiin (**4**), tetracyanothiophene (**7**) and tricyano-1,4-dithiino[c]-isothiazole (**6**), all of which are readily available from salt **1** or **2**. It has become evident that several new sulfur-containing heterocyclic compounds related to the cyanocarbons[4a,b] are accessible from

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(1) In this and subsequent papers in this series bold face arabic numerals are employed to name chemical structures, as suggested by L. F. Fieser and M. Fieser, "Style Guide for Chemists," Reinhold Publishing Corp., New York, N. Y., 1960, p. 66.

(2) G. Bähr and G. Schleitzer, *Ber.*, **88**, 1771 (1955); **90**, 438 (1957); G. Bähr, *Angew. Chem.*, **68**, 525 (1956).

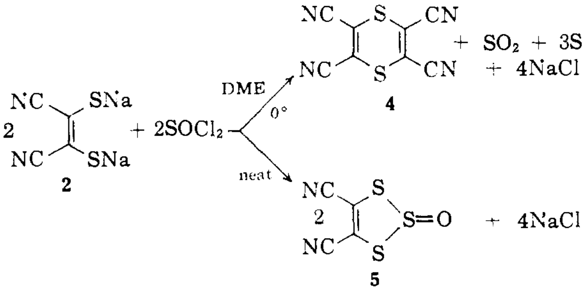
(3) (a) II, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962); (b) III, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *ibid.*, **84**, 4772 (1962); (c) IV, H. E. Simmons, D. C. Blomstrom and R. D. Vest, *ibid.*, **84**, 4782 (1962).

(4) (a) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick and W. J. Middleton, *ibid.*, **79**, 2340 (1957). (b) See series beginning T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middle-

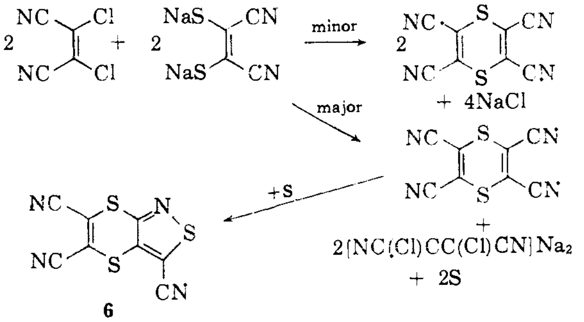
salts **1**, **2** and **3**, and these compounds have been generally termed for convenience, thiacyanocarbons, *i.e.*, salts and covalent compounds containing only carbon, nitrogen and sulfur and a plurality of cyano groups.

Synthesis of Thiacyanocarbons.—In a recent communication Bähr[5] has reported the oxidation of salt 2 with iodine to give tetracyano-1,4-dithiin. The products and mechanisn of the oxidation of salts **1**, **2** and **3** have also been under investigation in our laboratory. When salt **2** was treated with any of a wide variety of oxidizing agents. tetracyano-1,4-dithiin (**4**) was obtained in moderate to quantitative yields. Oxidants which gave **4** include chlorine in 1,2-dimethoxyethane (DME) (80%), perchlorylfluoride in DME (88%), iodine in aqueous potassium iodide solution (45%), thionyl chloride in DME (100%), sulfuryl chloride in DME (59%), sulfur monochloride in DME (71%), sulfur dichloride in DME (76%), potassium ferricyanide in water (48%) and ammonium persulfate in water (32%). The oxidizing systems employed are tabulated in the Experimental Section. The reactions were generally carried out by introducing one equivalent of oxidizing agent into one equivalent of salt **2** in solution or suspension at 0°. Salt **2** is slightly soluble in 1,2-dimethoxyethane and acetonitrile, and these solvents have proved valuable for carrying out many reactions of salts in this series where an aprotic medium is desired.

Thionyl chloride is a convenient reagent for the laboratory preparation of **4** from **2** in that nearly quantitative yields of the dithiin can be obtained in a high state purity. Salt **2** reacted with thionyl chloride in the absence of solvent to yield dicyanotrithiole-2-oxide (**5**),[5] a crystalline compound of limited stability whose role in the thionyl chloride oxidation will be discussed in paper III.



In an attempt to carry out a metathetical reaction of salt **2** and dichloromaleonitrile, tetracyano-1,4-dithiin ($C_8N_4S_2$) was obtained in 31% yield, but the major product (52%) was a new thiacyanocarbon, tricyano-1,4-dithiino[c]isothiazole (**6**) ($C_8N_4S_3$), which contains the virtually unknown isothiazole ring system. It was determined that although some dithiin **4** may be formed in a metathetical displacement reaction, dichloromaleonitrile functions primarily as an oxidizing agent as evidenced by the formation of elemental sulfur.[3b] Isothiazole **6** has also been detected in other oxidations of salt **2** (and **1**), and it will be shown below how **6** arises from a subsequent reaction of dithiin **4** with sulfur formed when salt **2** undergoes oxidation.



Large scale preparations of dithiin **4** and isothiazole **6** can be carried out by the direct oxidation of dimethylformamide solutions of sodium cyanide and carbon disulfide (*i.e.*, salt **1**) with chlorine and iodine, respectively, depending on the reaction conditions. The need for isolating and purifying[2,5] **2** is thus obviated.

Some insight into the conditions that lead to the formation of **6** can be gotten from the following observations. When sodium cyanodithioformate (**1**) was treated with one mole of chlorine in cold dimethylformamide solution and the reaction mixture was worked up after standing 24 hours, pure dithiin **4** was isolated in 51.5% yield (crude yield 80%) along with 6.5% of isothiazole **6**. In a similar experiment in which the reaction mixture was worked up as soon as chlorine addition was complete, the yield of purified **4** was 54.5% and no **6** was detected. Immediately after rapid addition of iodine in acetonitrile solution to **1**, only dithiin **4** was present, but after 24 hours, the reaction mixture contained a 45% yield of isothiazole **6** and no dithiin **4**.

The relationship between oxidations of salts **1** and **2** are reported in detail later.[3b] For the present purposes, however, we need only be concerned with some over-all observations.

The iodine oxidation could be studied conveniently by following changes in the ultraviolet spectrum when iodine was added to an acetonitrile solution of disodium dimercaptomaleonitrile (**2**). Salt **2** has limited solubility in acetonitrile, and at the point solution was complete (0.5 mole iodine added) the spectrum revealed only the disulfide salt **21**[3a] and dithiin **4**. When 0.75 mole of iodine had been added, the product was a mixture of **4** (increased) and **21** (decreased) and no isothiazole **6** was detected. After 1.0 mole of iodine had been added, only absorptions due to **4** were observed. The reaction mixture was allowed to stand overnight, and only isothiazole **6** was isolated (96%). Similarly it was shown that oxidation of salt **21** with iodine in DME gave isothiazole **6** as the only product after 24 hours.

These experiments and other observations[3b] proved that isothiazole **6** ($C_8N_4S_3$) was being formed from **4** ($C_8N_4S_2$) and elemental sulfur in a reaction unrelated to the initial oxidation reaction. When dithiin **4** was stirred with sulfur in the presence of sodium iodide and iodine under the reaction conditions, isothiazole **6** was formed in 59% yield.

ton, R. M. Scribner, C. W. Theobald and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(5) G. Bähr, *Angew. Chem.*, **70**, 606 (1958).

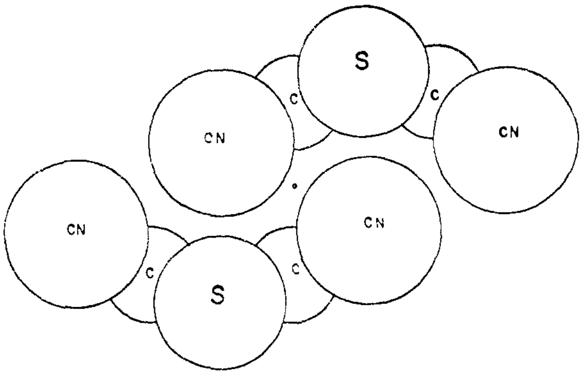
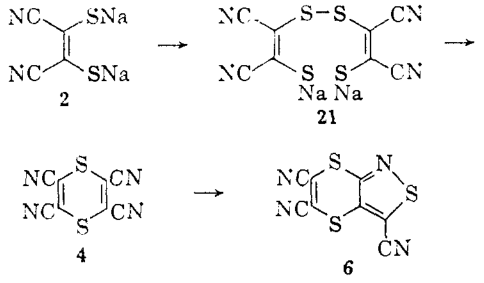


Fig. 1.—Molecular packing in crystals of tetracyano-1,4-dithiin as determined by preliminary X-ray analysis.

Sodium ethoxide catalyst in ethanol containing one mole of sulfur caused the conversion of **4** to **6** in 60% yield. Other anions were similarly effective in this transformation whose mechanism is discussed below.



It is interesting to recall that oxidations of salts **1** and **2** with chlorine gave predominantly dithiin **4**, whereas comparable oxidations with iodine gave largely **6** in similar periods of time. These observations are in accord with the mechanism suggested below for the insertion reaction which involves generation of species such as $X{-}S_7{-}S^-$ by attack of a nucleophile X^- on sulfur. Thus, the more nucleophilic iodide ion might be expected to show a faster rate for the over-all insertion process than chloride ion.

When dithiin **4** was heated at its melting point (207–208°), one mole of sulfur was exothermically expelled with the formation of the new tetracyanothiophene (**7**) in nearly quantitative yields.

7

The large scale preparation of **7** was best carried out in solvents, *e.g.*, 1,2,4-trichlorobenzene, at reflux, and yields as high as 85% were obtained. The synthesis of thiophenes by the pyrolysis of substituted dithiins has been discussed previously by Parham.[6]

Tetracyanothiophene (7), a colorless, crystalline solid, m.p. 198.5–199.5°, is the first example of a percyano aromatic compound. It is readily sublimed, soluble in polar solvents and possesses remarkable thermal stability. It was recovered unchanged after being passed at atmospheric pressure over quartz chips heated at 900° (contact time *ca.* 1.5 sec.). Like tetracyanoethylene,[7] **7** is a π-acid and shows characteristic charge-transfer spectra with aromatic hydrocarbons.[8]

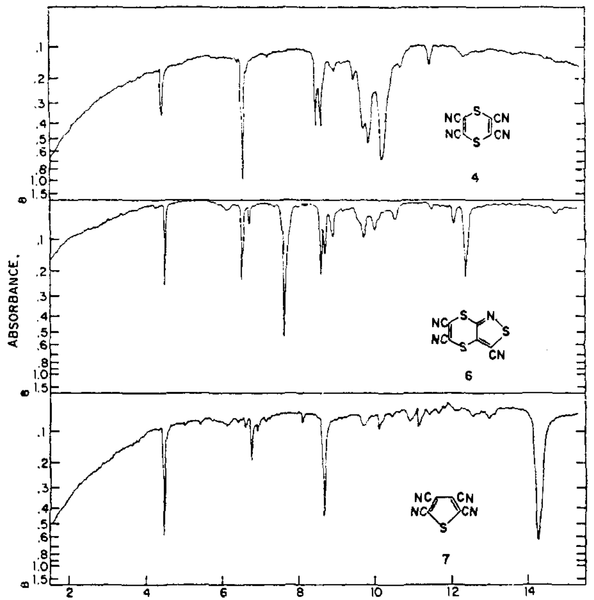


Fig. 2.—Infrared spectra: (**4**) tetracyano-1,4-dithiin, (**6**) tricyano-1,4-dithiino-[c]-isothiazole and (**7**) tetracyanothiophene, in methylene chloride.

The infrared spectrum of tetracyanothiophene in KBr shows only three strong bands at 4.49 (conj. $C{\equiv}N$), 8.68, and 14.29 μ. Weak aromatic absorption occurs at 6.76 μ. The ultraviolet spectrum of **7** shows two maxima at 239 (ϵ 24,600) and 281 mμ (ϵ 10,850) in methylene chloride.[9] The infrared and ultraviolet spectra of **4**. **6** and **7** are given Figs. 2 and 3, respectively.

Thiophene **7** readily undergoes characteristic nitrile reactions. Hydrolysis in 0.1 *N* sodium hydroxide solution at 40° gave the tetraamide **8** in 71% yield, while hot concentrated sulfuric acid gave the imide–diamide **9** in 87% yield. A suspension of **7** in concentrated hydrochloric acid was converted smoothly at 25° to the dicyanodiamide **10** in 80% yield, while hot concentrated hydrochloric acid gave a 53% yield of thiophenetetracarboxylic acid (**11**).[10]

The tetraacid **11** is most readily prepared by heating dithiin **4** under reflux in concentrated

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[6] (a) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **76**, 4960 (1954); (b) **77**, 68 (1955); (c) W. E. Parham, I. Nicholson and V. J. Traynelis, *ibid.*, **78**, 850 (1956); also see W. Kirmse and L. Horner, *Angew. Chem.*, **69**, 721 (1957); (d) W. E. Parham in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Editor, Pergamon Press, New York, N. Y., 1961, p. 248.

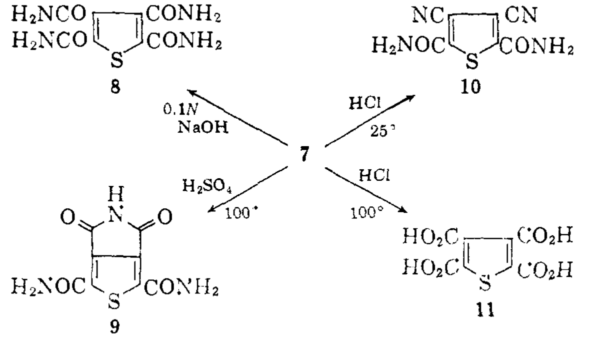
[7] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[8] Spectral studies of complex formation of **4**, **6** and **7** with π-bases and the derived equilibrium constants will be reported in subsequent papers. The three new thiacyanocarbons are weaker π-acids than tetracyanoethylene and are similar to quinones in this respect.

[9] Thiophene has λ_{max} 235 mμ (ϵ 4500) in hexane.

[10] Tetramethyl thiophenetetracarboxylate has been reported from the reaction of dimethyl acetylenedicarboxylate and sulfur; A. Michael, *Ber.*, **28**, 1633 (1895). Recently, H. Hopff and J. v. d. Crone, *Chimia*, **13**, 107 (1959), have saponified this product to obtain thiophenetetracarboxylic acid, whose properties agree with those of the acid prepared in our work.

hydrochloric acid. It was shown that hydrolysis occurred rapidly to give dithiin dicarboximide **13** (see below) which subsequently underwent slow hydrolysis accompanied by desulfurization to give tetraacid **11**. Structure **9** was assigned on the basis that a single product was obtained in high yield which contained an imide ring, and structure **10** was inferred from the expectation that acid functions are more rapidly hydrolyzed in the 2-position in thiophene than in the 3-position.[11]



Tetracyano-1,4-dithiin (4) is a pale yellow crystalline solid, m.p. 207–208° dec., which is stable in air and light when pure. The infrared spectrum of **4** exhibits bands at 4.46 (sh. 4.44) (conj. C≡N) and 6.57 μ (C=C) and shows only five other major absorptions. The ultraviolet spectrum has maxima at 244 (ε 16,600), 278 (ε 7,130), 317.5 (ε 5,620) and 332 mμ (ε 7,130) in methylene chloride.

1,4-Dithiin[12] has been shown by X-ray crystallographic studies to have a 2-fold axis and two planes of symmetry (C_{2v}).[13] The angle between the symmetry planes is 137° and < C—S—C = 100°, < C=C—S = 124°, (C—S) = 1.78 ± 0.05 Å., (C=C) = 1.29 ± 0.05 Å. With this background and since the molecular configuration is sufficiently non-spherical to limit placing of the molecules in the unit cell, a brief X-ray examination of tetracyano-1,4-dithiin was undertaken.[14] Crystals of **4** grow as flat plates and prisms. Precession and Weissenberg photographs (CuK_α) gave the tetragonal unit cell dimensions: a_0 7.00 ± 0.05. c_0 18.44 ± 0.04. With four formula weights per unit cell, the calculated density is 1.59 g./cc. (observed by flotation, 1.588 g./cc.). The space group was uniquely fixed as D_{4h}^4-$P4/nnc$. A chair conformation of the ring of **4** is very unlikely, and a boat conformation, as found for the parent 1,4-dithiin,[13] seems required. A staggered cup arrangement (see Fig. 1) satisfies the very efficient packing (high density) and the stringent symmetry requirements of the unit cell.

The dipole moment of tetracyano-1,4-dithiin measured in dioxane solution[15] was 4.0 ± 0.5 D., a value in accord with the conformation suggested by the X-ray studies. The dihedral angle in tetracyano-1,4-dithiin can be estimated from the measured value of the dipole moment and the group moments discussed in paper II.[8a] In this manner a dihedral angle of 130° was calculated, which agrees well with the boat geometry expected in the tetracyano derivative. A similar value was found for 1,4-dithiin.[13]

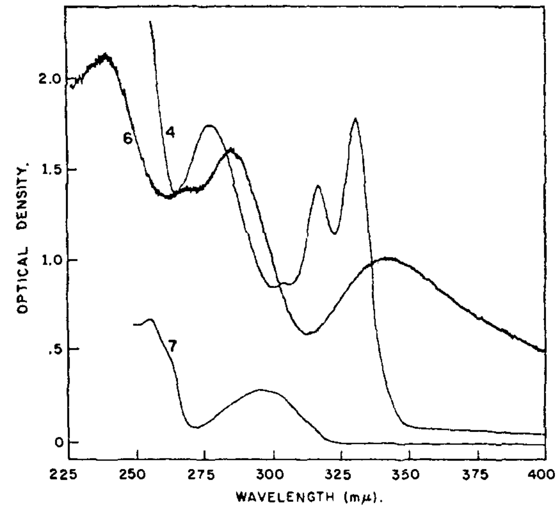
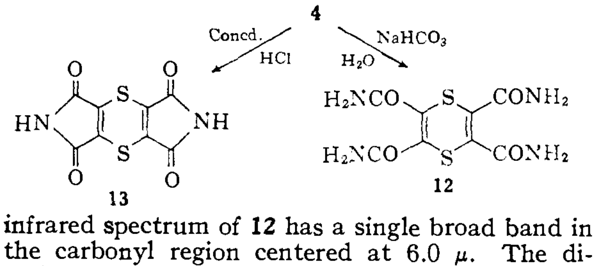


Fig. 3.—Ultraviolet spectra: (4) tetracyano-1.4-dithiin, (6) tricyano-1,4-dithiino-[c]-isothiazole and (7) tetracyanothiophene, in methylene chloride.

Tetracyano-1,4-dithiin does not possess aromatic properties, and its nitrile groups undergo normal hydrolysis in aqueous systems. Boiling water and cold dilute aqueous sodium hydroxide dissolved **4** to give orange solutions from which no definite products were isolated on acidification. Dilute aqueous sodium bicarbonate effected solution of **4**, and on acidification the impure tetraamide **12** could be isolated. Hydrolysis of a suspension of **4** in concentrated hydrochloric acid at 25° gave the dicarboximide **13** (96%) and tetraamide **12** (2%). The tetraamide **12** was formed in 75% yield when **4** was dissolved in concentrated sulfuric acid and the resulting solution poured on ice. It seems reasonable that **12** is the intermediate first formed in the hydrochloric acid hydrolysis of **4** to **13**, since the tetraamide **12** was smoothly converted to dicarboximide **13** when **12** was dissolved in cold concentrated hydrochloric acid. Methanolic sodium methoxide also effected the loss of ammonia from **12**, and **13** was isolated in 38% yield.

The tetraamide **12** is yellow and has an ultraviolet spectrum similar to that of dithiin **4**. The infrared spectrum of **12** has a single broad band in the carbonyl region centered at 6.0 μ. The dicarboximide **13** crystallized from acetic acid as



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[11] See W. Steinkopf, "Die Chemie des Thiophens," Verlag von Theodor Steinkopff, Dresden, 1941, p. 85. This might also be inferred from the ionization constants of thiophene-2-carboxylic acid (3.16 × 10^{-4}) and thiophene-3-carboxylic acid (7.8 × 10^{-5}); also see R. Roger and D. Nelson, *Chem. Revs.*, **61**, 179 (1961).

[12] W. E. Parham, H. Wynberg and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065 (1953).

[13] P. A. Howell, R. M. Curtis and W. N. Lipscomb, *Acta Cryst.*, **7**, 498 (1954).

[14] The authors are indebted to Dr. P. Arthur and Mr. K. R. Babcock for these studies.

[15] The authors wish to thank Professor M. Kreevoy, University of Minnesota, for communicating this result to them.

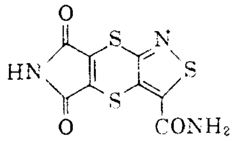
green plates of metallic luster, and **13** was typically acidic having pK_{A_1} 4.56 and pK_{A_2} 8.17 in 52.5% dimethylformamide. The infrared spectrum of **13** shows three bands in the carbonyl stretching region at 5.62, 5.75 and 5.86 μ. Solutions of **13** in water, ethanol, acetic acid, dimethylformamide, dimethyl sulfoxide, acetone and ethyl acetate are deep purple in color due to a broad band at 550 mμ (ε 86) which extends over most of the visible spectrum. The color of **13** is unusual in view of the lack of color of 1,4-dithiin[12] and pyromellitimide.[16] N-Ethylmaleimide is colorless and shows λ_{max} 310 mμ (ε 510) and two bands characteristic of the imide at 5.84 and 6.27 μ in the infrared.[17] Recently, N-(2,4-dinitrophenyl)-maleimide has been described[18] as a highly colored compound, although no ultraviolet spectral data were given. This maleimide showed characteristic imide absorption at 5.71 and 6.17 μ. It is probable that the long wave length bands responsible for the color of the latter compound as well as those of the dicarboximide **13** are charge-transfer absorptions both in the solid state and solution.

Tricyano-1,4-dithiino[c]isothiazole (6),[19] m.p. 181–182°, crystallizes as bright yellow needles from benzene. The infrared spectrum of **6** exhibits bands at 4.49 (conj. C≡N) and 6.51 μ (C=C). A strong absorption at 7.63 μ appears to be characteristic of a carbon–nitrogen stretching vibration associated with the isothiazole ring.[20] The ultraviolet spectrum of **6** has four bands at 342 (ε 4960), 285 (ε 7900), 268(sh) (ε 6860), and 238 mμ (ε 10,920). The absorption at 285 mμ (ε 7900) is similar to that observed in many simple isothiazoles,[20] and the remainder of the spectrum is similar to that of dithiin **4**.

In physical and chemical properties dithiin **4** and thiophene **7** are typically olefinic and aromatic, respectively, and the isothiazole **6** exhibits properties of an intermediate nature. The thiophene shows high thermal stability and the dithiin readily loses an atom of sulfur above 200° to give the thiophene. The isothiazole, however, is stable in the melt at 300°.

A U.S. Patent[19] recently reported that oxidation of sodium cyanodithioformate (**1**) with various reagents gave a compound claimed to be tetracyano-1,2,5-trithiepin (**14**), whose structure is isomeric with isothiazole **6**. Repetition of this procedure gave a compound whose chemical and physical properties were identical with those of our **6**. That the isothiazole structure is correct is based on the infrared and ultraviolet spectra, hydrolysis to a nitrile-free imide-amide and finally by ^{13}C n.m.r. spectral studies.

When **6** was stirred at 25° in concentrated hydrochloric acid suspension, there resulted in 63% yield an orange imide-amide whose infrared and ultraviolet spectra were in complete accord with those expected of structure **15**. The infrared spectrum of **15** showed no nitrile absorption and a complicated



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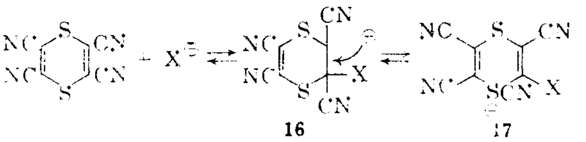
carbonyl region with bands at 5.62, 5.80, 5.87 and 6.00 μ. Comparion of the carbonyl region of **15** with that of dicarboximide **13** clearly revealed the presence of the carboximide ring fused to the dithiino ring. The ultraviolet spectrum of **15** was very similar to that of isothiazole **6**.

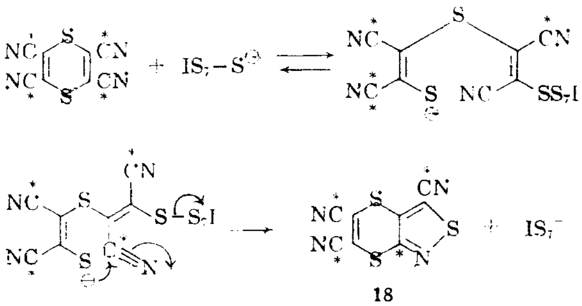
Direct evidence was found that the structure of the sulfur insertion product was isothiazole **6** and not proposed[19] trithiepin **14** by the following study.

The double bonds of dithiin **4** are very susceptible to addition–elimination reactions by nucleophiles with ring opening. Characterization of stable salts of type **17** (to be reported later) has suggested that ring opening of intermediate **16** occurs to give *trans* orientation of two cyano groups in **17** as shown. The sulfur insertion reaction catalyzed by iodide ion (and ethoxide ion) can then be interpreted in the following way. Nucleophilic attack on S_8 to give species analogous to $IS_7{-}S^-$ is well known.[21] Elimination with ring opening to an intermediate **17** (X = $S{-}S_7I$), followed by addition of the mercaptide ion to the α-cyano group forming five- and six-membered rings as shown, is now postulated. If elimination to give a *cis* arrangement of cyano groups had occurred, the trithiepin **14**[19] would have been a likely structure for the sulfur insertion product $C_8N_4S_3$.



16 **17**

$$I^{\ominus} + S_8 \rightleftharpoons IS_7{-}S^{\ominus}$$



18

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(16) E. A. Lawton and D. D. McRitchie, *J. Org. Chem.*, **24**, 26 (1959).

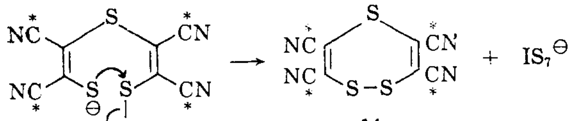
(17) K.-C. Tsou, R. J. Barrnett and A. M. Seligman, *J. Am. Chem. Soc.*, **77**, 4613 (1955).

(18) G. D. Clark-White and H. C. Robinson, *J. Chem. Soc.*, 2810 (1961).

(19) A compound described as tetracyano-1,2,5-trithiepin, prepared by oxidation of salt 1 with various oxidizing agents, has been reported in U. S. Patent 3,000,780, E. Merck Akt. (Germany). This structural characterization is shown below to be in error and the correct structure is isothiazole 6.

(20) Evidence for this assignment and absorptions characteristic of isothiazoles in the ultraviolet region will be published later.

(21) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956). Also see excellent reviews by M. Schmidt, *Angew. Chem.*, **73**, 394 (1961), and by O. Foss in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Editor, Pergamon Press, New York, N. Y., 1961, p. 83.

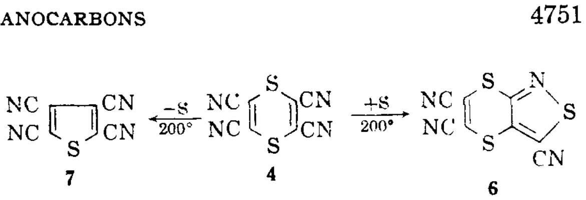


14

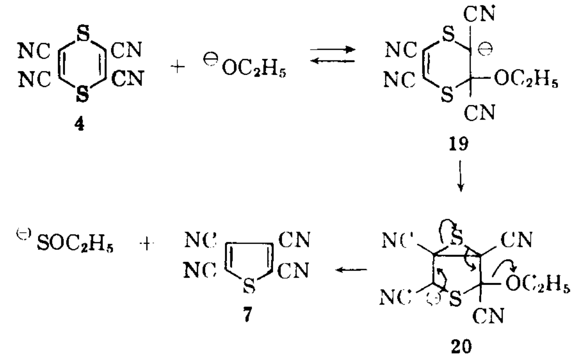
These alternatives were investigated by a study of the ^{13}C n.m.r. spectrum of the sulfur insertion product prepared from K^{13}CN (enriched to 65% ^{13}C). Labeled potassium cyanide was allowed to react with carbon disulfide in dimethylformamide and the reaction mixture was oxidized with iodine. Dithiin **4** which formed contained ^{13}C-atoms only in the nitrile groups as shown by the starred atoms in the above equations. The dithiin was converted directly in the reaction mixture by sulfur and iodide ion to the final product, which would have the distribution of the heavy isotope shown (**18**) if the mechanism and structure are correct.

A compound of structure **14** should show two closely spaced, equally intense $^{13}C{\equiv}N$ absorptions and **18** should show three nitrile peaks and a peak at considerable lower field due to $>C{=}N{-}$.[22] The spectrum of the isolated product consisted of three peaks at +37.8 (wt. 1), +81.3 (wt. 2) and +83.9 p.p.m. (wt. 1), relative to $^{13}CS_2$. Although little is yet known concerning nitrile shifts, acetonitrile shows a single peak for the nitrile carbon atom at $\delta_C = +73$ p.p.m. The peak of weight 2 at +81.3 p.p.m. is due to the two nitrile groups on the dithiino ring in **18**, since they experience nearly the same shielding. The peak of weight 1 at +83.9 p.p.m., also in the nitrile region, was assigned to the nitrile group on the isothiazole ring, which is predicted to appear at higher field.[22] The single absorption at +37.8 p.p.m. can be assigned to the ring junction carbon. Assuming that sulfur atoms are roughly equivalent to carbon atoms (the α- and β-carbons in thiophene have almost identical shifts),[22] the predicted shift should be similar to that found for the α-carbons in pyridine ($\delta_c = +43.1$ p.p.m.). Allowance for the known effect of adding a carbon side chain or condensed aromatic ring (both cause a shift to lower field of about 8 p.p.m.) gives a predicted shift in **18** of +35 p.p.m. The excellent agreement with that found ($\delta_C = +37.8$ p.p.m.) is probably fortuitous, but the over-all spectrum is in complete accord with that expected of structure **18**.

Interconversion Reactions of Dithiin 4, Isothiazole 6 and Thiophene 7.—Elemental sulfur is both lost and added thermally by dithiin **4**. When **4** was heated to 200°, one mole of sulfur was expelled exothermically and sublimed from the melt giving thiophene **7** in nearly quantitative yield. When **4** was melted in the presence of added sulfur no **7** was detected, isothiazole **6** was isolated in 15% yield, and the major products were of high molecular weight. The mechanism by which sulfur is expelled thermally as the element from substituted dithiins is unknown, but it seems clear on the basis of energetics that monatomic sulfur cannot be involved. The thermal insertion reaction (**4**→**6**) possibly involves free radical intermediates similar in structure to the anion **17** ($X = -S_8$).



Disproportionation of **4** to a mixture of **6** and **7** was effected at lower temperatures by certain nucleophiles. Dithiin **4** is stable at prolonged reflux in dry ethanol, but ethoxide ion, either added or generated *in situ*, caused the interconversion reaction. The addition of a catalytic amount of urea (known to generate ethoxide ion) brought about the conversion of **4** to **6** in 56% yield in 2 hours at reflux. When **4** was boiled in absolute ethanol containing a catalytic amount of sodium ethoxide, it was slowly converted to a mixture of thiophene **7** (1%) and isothiazole **6** (27%). It is known from other experiments that **7** is rapidly degraded by bases and is recovered only in poor yield from ethanol solutions containing sodium ethoxide. This observation accounts for the low yield of **7** in the disproportionation reaction. The following scheme rationalizes these results in terms of an addition–elimination mechanism. The conversion **19**→**20** probably competes with the ring-opening elimination. Similar bridging structures have been invoked previously to account for the reactions of the dithiin system.[23,24]



As sulfur species such as $^{-}S_xOC_2H_5$ are released in solution, rapid reaction with dithiin **4** to give isothiazole **6** is expected by a path completely analogous to that suggested above for the iodide ion-catalyzed insertion of externally added sulfur. Dithiin **4** was treated with an ethanol solution

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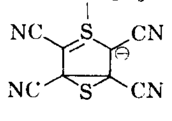
[22] The ^{13}C n.m.r. spectrum was kindly determined by Dr. P. C. Lauterbur, Mellon Institute, and we gratefully acknowledge his helpful interpretation of the spectrum.

(23) W. E. Parham, E. T. Harper and R. S. Berger, *J. Am. Chem. Soc.*, **82**, 4932 (1960).

(24) Displacement by ethoxide ion at sulfur, especially in a negatively substituted system, is a reasonable competitive alternative to the addition reaction to give **19**. Such intermediates, presumably of type i, can be carried through a scheme similar to **19** → **20** → **7**. Direct displacement on sulfur is well known in negatively substituted disulfides (see A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 589 (1959)). However, since the addition–elimination sequence by several anions with dithiin **4** has now been established, the scheme **19** → **20** → **7** is preferred.



i

containing a catalytic amount of sodium ethoxide and one mole of added sulfur. The yield of isothiazole increased to 60% and no thiophene could be isolated.

Polarographic Studies.—Diffusion current *vs.* concentration studies were made of **4**, **6** and **7**. Two well-defined reduction waves were obtained for tetracyano-1,4-dithiin (**4**) in 50% aqueous acetic acid. The half-peak potentials ($E_{p/2}$), measured *vs.* a saturated calomel reference electrode, were −0.24 and −0.72 v. in 50% aqueous acetic acid and −0.23 and −0.79 v. in 50% aqueous acetic acid containing 0.1 M sodium acetate. Other studies in these laboratories have shown that neither 1,4-dithianes nor cyano groups are polarographically reducible in the systems employed. It is therefore apparent that the reduction is associated with the ethylenic bonds in the molecule. By application of the Ilkovic equation to the over-all reduction using 6×10^{-6} cm.^{2}/sec. as an approximate diffusion coefficient for **4** (a value frequently found for many ions and organic molecules),[25] values of 6.07 and 4.17 (6 and 4) electrons were obtained for the number of electrons involved in the reduction in 50% acetic acid and 50% acetic acid containing 0.1 M sodium acetate, respectively. These values for the number of electrons must be regarded as tentative until further data are available to determine whether the currents measured are due to kinetic effects in the vicinity of the dropping mercury electrode.

Similar studies were made of tetracyanothiophene (**7**) and tricyano-1,4-dithiino[c]isothiazole (**6**) in 50% aqueous acetic acid. The thiophene **7** showed two well-defined reduction waves (−0.7 and −1.0 v.) similar to **4**, both waves exhibiting a linear relationship between concentration and diffusion current. The reduction of the isothiazole **6** was, however, less well defined. The first reduction occurred at $E_{p/2}$ −0.4 v., and the second wave (or waves) at approximately −0.7 v. These results are summarized in Table I.

TABLE I

POLAROGRAPHIC STUDIES[a]

Compound	$E_{p/2}$ (v.)[b]	i_{d_1}/i_{d_2}[c]
4	−0.24	1:2
	− .70	
7	− .70	1:1
	−1.0	
6	−0.40	
	−0.70	
	−1.0[d]	

[a] The reductions were carried out in 50% aqueous acetic acid containing 0.005% Triton X-100 (dropping mercury *vs.* saturated calomel electrode) at 25°. [b] The values for each compound correspond to the first, second, etc., waves. [c] Diffusion current ratios for first and second waves. [d] Uncertain. [e] Merges with cut-off and could not be accurately measured.

The ease with which the first reduction occurs in tetracyano-1,4-dithiin is striking compared to tetracyanothiophene and probably reflects the aromatic character of the latter compound. It would appear that $E_{p/2}$ of the former is not affected by pH (based on runs at only two pH's, with and without added sodium acetate), which would indicate that only electron transfer is involved in the first step of the reduction. The over-all reduction, which appeared to correspond to a 4-electron transfer, probably is accounted for solely by the two double bonds in **4**.

Acknowledgment.—The authors are pleased to acknowledge the assistance of Miss Lucille Williams in carrying out and interpreting the polarographic studies.

Experimental[26]

Materials.—All commercial reagents were of high grade and were distilled or recrystallized, where necessary, before use. Sodium cyanodithioformate·3DMF (**1**)[2] and disodium dimercaptomaleonitrile (**2**)[2] were prepared by the indicated literature methods, and salt **2** was recrystallized from absolute ethanol and dried thoroughly. The impurities in salt **2** are usually sulfur, sodium cyanide and ethanol, and these were removed before use. Ethanol could be removed completely only by drying at 80° (<1 mm.) overnight. Otherwise, **2** gave low yields and erratic results in some of the reactions described in this work.

Tetracyano-1,4-dithiin (4). Oxidation of Salt 2 with Thionyl Chloride.—Salt **2** (200 g., 1.08 moles) was suspended in anhydrous DME (1 l.) in a flask equipped with a thermometer, magnetic stirrer and pressure equalized addition funnel. The apparatus was predried and protected from atmospheric moisture by a calcium chloride drying tube. The stirred suspension was cooled externally to 0° using a Dry Ice-acetone-bath which was more effective than wet ice for temperature control. A solution of distilled thionyl chloride (128 g., 1.08 moles) in DME (100 ml.) was added dropwise over 1 hour. During addition the mixture became orange, red and finally black. At the end of the addition the color faded to leave a pale yellow suspension. The mixture was allowed to warm to 25° and then was filtered by suction through a medium sintered-glass funnel. The solids were stirred (polythene spatula, since the mixture attacks some metals) and washed with DME (500 ml.). The combined filtrates were evaporated to dryness at 25°. (The solid collected on the filter was a mixture of sodium chloride and sulfur and contained no sodium sulfide. In separate experiments the yields of both inorganic products were determined to be nearly quantitative. The sulfur dioxide liberated in the reaction has a very high solubility in DME and was lost during evaporation.) The crystalline residue was pale yellow in color and melted at 200–205° dec. The yield of **4** at this stage was 117 g. (100%). Recrystallization from boiling toluene gave a total of 112 g. (96%) of pure tetracyano-1,4-dithiin (**4**), m.p. 207–208° dec., when subsequent crops were recovered.

Anal. Calcd. for $C_8N_4S_2$: C, 44.43; N, 25.91; S, 29.66. Found: C, 44.74; N, 25.71; S, 29.48.

Dithiin **4** may be stored indefinitely without decomposition and is soluble in acetone, ethyl acetate, dimethylformamide and DME. Its solubility is low in chloroform, ether and benzene. The best solvent for recrystallization is dichloroethylene, from which **4** can be obtained as large yellow prisms. The infrared spectrum of **4** is simple showing only seven major bands: 4.46 (conjugated CN, sh. at 4.44), 6.57 (C=C stretching), 8.49, 8.64, 9.75, 9.87 and 10.22 μ. The ultraviolet spectrum in methylene chloride shows maxima at 332 (ε 7130), 317.5 (ε 5620), 278 (ε 7130) and 244 mμ (ε 16600).

Other Oxidations of 2 to 4.—In general, salt **2** was oxidized to **4** by a large number of oxidants. In some oxidations isothiazole **6** was formed as a by-product, but this could be minimized by rapid work-up of the reaction mixtures. Most of the oxidations were carried out by introducing the oxi-

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[25] L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, p. 73.

[26] All melting points are corrected and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ). Spectra were obtained on pure liquids or in potassium bromide wafers. The visible and ultraviolet spectra were obtained by means of a Cary model 11 recording spectrophotometer. The experimental conditions under which the polarographic studies were made were conventional.[25]

dizing agent into a solution or a suspension of **2**, and the results are summarized in Table II. The reactions were worked up in conventional manners, either by direct filtration of the product or extraction with a suitable solvent. The yields refer generally to once-recrystallized products.

Reaction of 2 with Dichloromaleonitrile.—Salt **2** (22.2 g., 0.12 mole) was suspended in dry DME (300 ml.) and dichloromaleonitrile (17.4 g., 0.12 mole) was added in one portion while the mixture was stirred in an ice-bath under anhydrous conditions. Deep red color formation accompanied the mildly exothermic reaction. The reaction mixture was flushed with nitrogen, stoppered, and allowed to stir for 72 hours at 25°. The solids were removed by suction filtration and were shown to contain sodium chloride and sulfur. The filtrate was evaporated to dryness at room temperature and the dark residue was extracted with 300 ml. of warm benzene. The insoluble material (6 g.) was recrystallized from boiling benzene to give 4.0 g. (31%) of **4**, m.p. 207–208° dec. The benzene extract was evaporated to give 13.3 g. of crude **6**. Recrystallization from a small volume of benzene gave 7.8 g. (52%) of pure **tricyano-1,4-dithiino-[c]-isothiazole (6)** as bright yellow needles, m.p. 181–182°.

Anal. Calcd. for $C_8N_4S_3$: C, 38.69; N, 22.56; S, 38.74. Found: C, 38.67; N, 22.53; S, 38.58.

TABLE II

OXIDATIONS (**2** → **4**)

Oxidant[a]	Solvent[b]	Temp., °C.	Time, hr.[c]	Yield, %[d]
$SOCl_2$	THF	0	0.5	87
SO_2Cl_2	DME	0	.5	59
	CH_3CN	0	.5	60
	$CH_3CO_2C_2H_5$	0	.5	60
S_2Cl_2	DME	0	.5	71
	DME	0	.5	70[e]
SCl_2	DME	0	.5	76
Cl_2	DME	0	1.5	80[e]
Cl_2	DME	0	1.5	49
I_2, KI	H_2O	25	1.0	45
$K_3Fe(CN)_6$	H_2O	25	0.1	48
$FClO_3$	DME	0	2.0	88
$(NH_4)_2S_2O_8$	H_2O	25	1.0	32

[a] Orders and rates of additions were varied in some runs. [b] THF = tetrahydrofuran; DME = dimethoxyethane. [c] Optimum times were not determined but the reactions appeared to be complete at the end of the additions. [d] Yields are based on a 1:1 mole ratio of oxidant:**2**. [e] Run in the presence of a catalytic amount of added sulfur.

Isothiazole **6** stores indefinitely without decomposition and is soluble in acetone, ethyl acetate, dimethylformamide and DME. It is much more soluble in all of the usual solvents than **4**. The infrared spectrum of **6** is relatively simple, and the only major bands occur at 4.49 (conj. C≡N), 6.51 (C=C stretching) 7.65, 8.60, 8.69, 9.70 and 12.36 μ. The ultraviolet spectrum of **6** is similar to that of **4**. The maxima occur at 342 (ε 4960), 285 (ε 7900), 268 (ε 6860) and 238 mμ (ε 10920).

Dicyano-1,2,3-trithiole-2-oxide (5).—Salt **2** (0.5 g., 0.0029 mole) was ground for 2 minutes in a mortar with thionyl chloride (8 ml.). The mixture was filtered and the filtrate was diluted with 20 ml. of petroleum ether. The fine yellow needles which crystallized weighed 0.07 g. (14%). An analytical sample of **5** was obtained by sublimation *in vacuo* at 100–105°.

Anal. Calcd. for $C_4N_2OS_3$: C, 25.54; S, 51.00. Found: C, 25.43; S, 50.93.

Trithiole oxide **5** can be stored for several weeks under nitrogen at room temperature without decomposition. The infrared spectrum shows conjugated nitrile absorption at 4.50 μ, (C=C) stretching at 6.60 μ, and (S=O) at 9.55 μ.

Preparation of Dithiin 4 by Direct Oxidation of Sodium Cyanodithioformate (1).—A well-supported 3-l., three-necked flask was equipped with a mechanical stirrer, reflux condenser with a thermometer internally suspended, addition funnel and a large cooling bath. A suspension of sodium cyanide (196 g., 4.00 moles) in DMF (1800 ml.) was stirred while carbon disulfide (304 g., 4.00 moles) was added dropwise at a rate of *ca.* 100 g./hr. The reaction mixture was allowed to warm spontaneously to 55° and then kept at 50–60° by adjusting the rate of carbon disulfide addition. In some runs it was necessary to cool the reaction flask with ice to maintain a temperature below 60°. After the addition was complete, the dark reaction mixture was stirred at 55° for 1 hour; the stirrer blade was then raised above the liquid level, and the mixture was allowed to cool overnight. A thick crystalline mass formed on cooling.

The addition funnel was replaced with a gas inlet tube which terminated above the level of the mixture. The reaction flask was cooled in an ice-bath and the stirrer was turned on and lowered as far as possible into the semi-solid mass. A slow stream of chlorine was introduced into the flask, and as the reaction proceeded the crystalline mass slowly liquefied. Over 2 hours the mixture became red and then yellow. When no further change in color was observed, the addition of chlorine was stopped and 40 g. of Celite was added to the mixture. The inorganic solids (sulfur and sodium chloride) were removed by filtration through a Buchner funnel. The solids were washed with acetonitrile (50 ml.) and the combined washings and filtrate were poured into water (10 l.) with vigorous stirring. The crude product which precipitated was collected by suction filtration, washed thoroughly with water and air-dried. The crude dithiin **4** (174 g., 80%) melted at 180–210° and was found to be of at least 90% purity by ultraviolet spectral analysis. Recrystallization of the crude product from ethylene dichloride gave 111 g. (51.5%) of pure **4**, m.p. 207–214° dec. The filtrates were evaporated to dryness and extracted with carbon disulfide to remove 10.1 g. of sulfur. The carbon disulfide-insoluble residue was recrystallized from benzene–methylcyclohexane to give 15.7 g. (6.5%) of isothiazole **6**, m.p. 181–183°.

When the reaction was carried out on a smaller scale (0.5 mole of sodium cyanide), the filtration and isolation of **4** could be accomplished much more rapidly and the yield of recrystallized **4** was 54.5%. No isothiazole **6** was detected.

Oxidation of 2 with Iodine in Acetonitrile (Ultraviolet Study).—A solution of iodine (25.2 g., 0.10 mole) in acetonitrile (500 ml.) was added to a suspension of **2** (18.6 g., 0.10 mole) in acetonitrile (200 ml.) at 0°. The ultraviolet and visible spectra were taken at (a) the point where all of the salt had dissolved (*ca.* 0.50 equiv. of iodine); (b) 0.75 equiv. of iodine had been added; (c) iodine addition was complete; and (d) after stirring 12 hours at room temperature. The spectra were consonant with the following observations:

At (a) the intermediate salt **21** (388 mμ, sh. 425 mμ) was the major component although a fairly strong absorption at 247 mμ appeared in all of these spectra. Dithiin **4** absorbs strongly at 244 mμ.

Spectrum (b) was consistent with a mixture of **21** and **4**. The principal absorptions of **4** were observed at 246, sh. 279, 315 and 329 mμ, and the minor component of the mixture was **21**.

Spectrum (c) clearly showed the maxima of **4** (246, 329 mμ) and iodine (290 and 365 mμ).

Spectrum (d) showed iodine (290, 365 mμ), traces of **4** (247, 330 mμ) but no significant amount of isothiazole **6** and was in general rather complicated. In experiments carried out under the same conditions, however, **6** was the only product isolated.

Oxidation of 2 with Iodine in DME (Product Isolation).—Salt **2** (20 g., 0.108 mole) was added by means of a solid addition funnel to a solution of iodine (27.4 g., 0.108 mole) in DME (200 ml.) in a flask equipped with a magnetic stirrer, thermometer, and an addition funnel. During the addition, the temperature was maintained at 10–20° by external cooling. The addition was carried out in small portions over 6 hours under anhydrous conditions. The reaction mixture was worked up by evaporation to dryness, extraction of the solids with ethyl acetate, a second evaporation to dryness and benzene extraction of the residue. Evaporation of the benzene solution gave 13.3 g. (96%) of **6**, m.p. 175–180°, whose infrared spectrum was identical to that of an authentic sample. One recrystallization from benzene gave 13 g. of pure **6**, m.p. 181–182°.

Oxidation of *trans-trans*-21 with Iodine in DME.—A solution of *trans-trans*-**21** (3 g., 0.009 mole) in 25 ml. of DME was added over 3 hours to a suspension of iodine

(2.34 g., 0.009 mole) in 20 ml. of DME. When the addition was complete the solution was evaporated at 25° to give a dark tar. Extraction of this residue with hot benzene gave 1.05 g. of a semi-crystalline mass. After this product was washed with ether, there was obtained 0.64 g. of crystalline solid, m.p. 125–145° (28% crude yield). The infrared spectrum of this product showed it to be only slightly impure **6**.

Oxidation of Salt 1 with Iodine in Acetonitrile.—A suspension of salt **1** (103.2 g., 0.400 mole) in acetonitrile (200 ml.) was stirred at −20 to −10° while iodine (50.8 g., 0.200 mole) suspended in acetonitrile (1200 ml.) was added dropwise over 2 hours. The mixture became yellow and then red. After the mixture was stirred overnight at 25°, sulfur (13.6 g.) was removed by filtration, and the solvents were evaporated *in vacuo*. The residue was extracted with 2 l. of cold benzene and with 1 l. of boiling benzene. The combined extracts were washed with water to remove residual DMF. The benzene solution was dried over anhydrous sodium sulfate and concentrated to a volume of 200 ml. The solid was collected and recrystallized from hot benzene to give 9.1 g. (36%) of isothiazole **6**, whose properties were identical with those of previously prepared samples.

Tetracyanothiophene (7).—Dithiin **4** (110 mg., 0.00051 mole) was placed in a small test-tube which was then immersed in an oil-bath heated at 210–220°. The solid melted to a yellow liquid, and shortly thereafter an exothermic reaction occurred. Sulfur sublimed to the cooled portion of the tube during 10 minutes. The dark melt solidified on cooling, and the contents of the tube were washed onto a filter with carbon disulfide. After the residue was washed thoroughly with carbon disulfide it was sublimed to give colorless rods of pure **tetracyanothiophene (7)**, m.p. 198°, 92 mg. (98%).

Anal. Calcd. for C_8N_4S: C, 52.16; N, 30.42; S, 17.41. Found: C, 52.22; N, 29.58; S, 17.73.

The infrared spectrum of **7** was very simple and showed only three strong bands at 4.49 (conj. C≡N), 8.68 and 14.28 μ. Weak (C=C) stretching was evident at 6.60, 6.77 and 6.93 μ. The ultraviolet spectrum showed maxima at 281 (ε 10850) and 239 mμ (ε 24600).

The large scale preparation of **7** is best carried out in a solvent. Yields of about 70% of 99+% purity along with about 10% of 85% pure material can be readily prepared by the following procedure.

Dithiin **4** (10 g., 0.046 mole) was suspended in 50 ml. of dry 1,2,4-trichlorobenzene in a Minilab wide mouth reaction vessel fitted with a thermometer, stirrer and vent. The vessel was immersed in an oil-bath previously heated to 225°, and in 12–15 min. the internal temperature reached 195–200°. An exothermic reaction occurred and after an additional 3–5 min. the heating bath was removed. The reaction mixture was cooled and diluted with 5–6 volumes of petroleum ether and the solid removed by filtration. The crude product was extracted in a Soxhlet extractor with carbon disulfide for 4–5 hours to remove sulfur and other contaminants. In this operation only a small amount of **7** was dissolved. The carbon disulfide-insoluble residue was then extracted with ethyl acetate and the extract was evaporated to dryness. The crude tetracyanothiophene was dissolved in boiling benzene, about 100 ml./gram being required. The benzene solution was treated once with Darco and filtered. There was deposited 5.9 g. (70%) of pure tetracyanothiophene (**7**), m.p. 197–198°. An additional 0.9 g. of **7**, m.p. 195–196°, was obtained from the filtrate. This second crop was judged to be of approximately 85% purity by spectral analysis.

Thiophenetetracarboxylic Acid Tetraamide (8).—Compound **7** (0.20 g., 0.00109 mole) was stirred at 40° with 54.5 ml. of 0.100 *N* sodium hydroxide solution (0.00545 mole). Solution was complete within 30–45 minutes. The mixture was cooled and acidified with concentrated hydrochloric acid. On standing, a fine white solid precipitated. The solid was collected and washed with water, but no suitable solvent for recrystallization could be found. The yield of slightly impure **thiophenetetracarboxylic acid tetraamide (8)** was 0.20 g. (71%), m.p. 233–234°. The infrared spectrum showed bands characteristic of primary amide and was in accord with the assigned structure.

Anal. Calcd. for $C_8H_8N_4O_4S$: C, 37.50; H, 3.15; N, 21.87; S, 12.52. Found: C, 36.77; H, 2.94; N, 21.42; S, 12.66.

2,5-Dicarbamoyl-3,4-thiophenedicarboximide (9).—Compound **7** (0.40 g., 0.0022 mole) was mixed with 3 ml. of concentrated sulfuric acid in a small flask. During the solution process the mixture warmed spontaneously to 40° followed by a more rapid evolution of heat which carried the temperature to 55–60°. The solution was heated with a free flame to 100° and then rapidly cooled. When the resulting solution was poured into 30 ml. of ice-water, a fine white solid precipitated and was collected, washed with water and dried. The yield of essentially pure product was 0.45 g. (87%). The product was further purified by solution in 30 ml. of dimethylformamide on a steam-bath followed by dilution of the cooled solution with 50 ml. of methylene chloride. Pure **2,5-dicarbamoyl-3,4-thiophenedicarboximide (9)** was obtained as a white micro-crystalline solid, m.p. >300°. The infrared spectrum of **9** showed amide (NH_2) at 2.95–3.12 μ, imide carbonyl at 5.67 and 5.80 μ, amide carbonyl at 5.90–5.97 μ, amide (NH_2) at 6.15 μ and thiophene (C=C) at 6.47 μ.

Anal. Calcd. for $C_8H_5N_3O_4S$: C, 40.20; H, 2.11; N, 17.58; S, 13.42. Found: C, 40.22; H, 2.22; N, 17.16; S, 13.45.

3,4-Dicyano-2,5-thiophenedicarboxamide (10).—Compound **7** (0.50 g., 0.0027 mole) was suspended in 10 ml. of concentrated hydrochloric acid. The flask was stoppered and the mixture was stirred at 25°. A chalk-white suspension began to form in 4 hours. After 3 days the mixture was diluted with an equal volume of water, and the white solid was collected by suction filtration. The precipitate was washed with water and dried and weighed 0.48 g. (80%). Recrystallization from glacial acetic acid afforded 0.4 g. of pure **3,4-dicyano-2,5-thiophenedicarboxamide (10)**, m.p. >300°. The infrared spectrum showed characteristic amide absorption at 2.95, 3.00 and 3.15 μ. Amide carbonyl appeared at 5.95 μ and the nitrile groups absorbed at 4.45 μ. The ultraviolet spectrum had λ_{max} 272 mμ (ε 7920). The spectrum showed no evidence of intramolecular hydrogen bonding, and the product was assigned the 2,5-diamide structure.

Anal. Calcd. for $C_8H_4N_4O_2S$: C, 43.63; H, 1.83; N, 25.45; S, 14.57. Found: C, 43.69; H, 2.00; N, 25.25; S, 14.77.

Thiophenetetracarboxylic Acid (11).—Compound **7** (5.0 g., 0.027 mole) was heated under reflux for 8 hours in 100 ml. of concentrated hydrochloric acid. The white crystalline solid which separated on cooling to 0° was filtered, pressed free of solution and dissolved in 125 ml. of water. The aqueous solution was passed through a column of 80 g. of Amberlite IR-120 (strong acid resin). The eluate was evaporated *in vacuo*, and the residue was recrystallized from 10 ml. of water to give 3.75 g. (53%) of hard white needles melting at 253° dec. An analytical sample of **thiophenetetracarboxylic acid (11)** was obtained by drying the recrystallized product for 3 hours at 118° (1 mm.). The infrared spectrum was characteristic of a polycarboxylic acid.

Anal. Calcd. for $C_8H_4O_8S$: C, 36.92; H, 1.54; neut. equiv., 65.0. Found: C, 36.97; H, 1.80; neut. equiv., 65.8.

Thiophenetetracarboxylic acid was also prepared directly from tetracyano-1,4-dithiin. A suspension of dithiin **4** (0.50 g., 0.0023 mole) in concentrated hydrochloric acid (25 ml.) was stirred and heated under reflux for 48 hours. The mixture was filtered hot to remove 0.070 g. (95%) of sulfur. The filtrate was cooled to 0° and 0.49 g. (83%) of tetraacid **11**, m.p. 256–264° dec., deposited. The product was only slightly impure and was characterized by its infrared spectrum.

In a similar experiment dithiin **4** (5.0 g., 0.023 mole) was heated under reflux in concentrated hydrochloric acid (200 ml.). Small samples were removed at intervals during the course of the reaction and analyzed by their infrared spectra. After 1 hour, dithiin **4** could no longer be detected and conversion to dithiindicarboximide **13** seemed complete. Over the next 3 days the dicarboximide **13** slowly dissolved and sulfur precipitated. The product was worked up as described above to give 4.26 g. (72%) of tetraacid **11**, m.p. 265–270° dec.

1,4-Dithiindicarboximide (13).—Compound **4** (0.50 g., 0.0023 mole) was stirred in suspension in 10 ml. of concentrated hydrochloric acid at 25° in a stoppered flask. After 3 days the yellow crystalline tetranitrile was converted to a green solid. The solid was collected by suction filtration and was washed with water. (The infrared spectrum of the crude product showed the absence of nitrile absorption. When the reaction was interrupted after 1 day the spectrum still showed considerable nitrile absorption.) The crude yield was 0.59 g. (100%). Attempted recrystallization from water gave dark solutions from which small amounts of the dicarboximide were obtained as green plates. Recrystallization of the bulk of the crude product from glacial acetic acid afforded complete recovery of **1,4-dithiindicarboximide** (13) as metallic green-bronze plates, m.p. >300° (black at 330°).

Anal. Calcd. for $C_8H_2N_2O_4S_2$: C, 37.80; H, 0.79; N, 11.02; S, 25.23; neut. equiv., 127. Found: C, 38.03; H, 0.94; N, 10.66; S, 25.40; neut. equiv., 114.

The infrared spectrum showed bands at 5.62, 5.75 and 5.86 μ characteristic of the maleimide structure. Sharp (N-H) occurred at 3.01 μ. Ring double bonds showed absorption at 6.36 μ. Solutions of **13** in acetic acid, ethanol, acetone, dimethylformamide and water were of a deep permanganate purple color. The ultraviolet spectrum in dimethylformamide showed maxima at 550 (ϵ 86), 420 (ϵ 1150) and 368 mμ (ϵ 3000). In ethanol, additional maxima were observed at 280 (ϵ 3570) and 230 mμ (ϵ 17700). The dicarboximide was acidic, having pK_{A_1} 4.56 and pK_{A_2} 8.17 in 52.5% dimethylformamide (by volume).

When the hydrochloric acid filtrate from the original reaction mixture was diluted with water, a small amount of highly crystalline yellow plates formed. In large-scale runs this minor product was isolated in 2% yield and could be purified by solution in concentrated hydrochloric acid followed by dilution with water. **1,4-Dithiintetracarboxamide** (12) was obtained as bright yellow prisms, m.p. >350°. The infrared spectrum showed primary amide absorption at 3.00, 3.15 and 6.25 μ. The amide carbonyl absorbed at 6.00 μ.

Anal. Calcd. for $C_8H_8N_4O_4S_2$: C, 33.33; H, 2.80; N, 19.44; S, 22.25. Found: C, 33.13; H, 2.98; N, 19.77; S, 22.44.

1,4-Dithiintetracarboxamide (12).—The tetraamide is best prepared by controlled acid hydrolysis of **4**. A.-Dithiin **4** (1.00 g., 0.0046 mole) was stirred at 25° with 10 ml. of concentrated sulfuric acid. After 3 hours the bright orange solution was poured into a mixture of 50 g. of water and 50 g. of ice. The yellow solid which precipitated was removed by filtration and was washed thoroughly with water to give 1.31 g. of crude tetraamide, m.p. >320°. Purification was effected by dissolving the solid in a small volume of concentrated hydrochloric acid at room temperature, filtering and slowly diluting with cold water. The tetraamide **12** (1.0 g., 75%) crystallized as large yellow plates.

B.—Compound **4** (1.00 g., 0.0046 mole) was stirred with a solution of sodium bicarbonate (1.93 g., 0.023 mole) in 20 ml. of water. After 1 hour at 25° solution had occurred. The mixture was acidified with cold concentrated hydrochloric acid, and a dark solid precipitated. The solid (1.10 g., 83%) was partially purified by solution in base and reprecipitating with acid followed by solution in concentrated hydrochloric acid and dilution with water. There was obtained approximately 0.8 g. of **12**, which was still slightly impure judged by the infrared spectrum.

Conversion of Tetraamide 12 to Dicarboximide 13. A. Hydrochloric Acid.—Tetraamide **12** (1.44 g., 0.0050 mole) was stirred in 35 ml. of cold concentrated hydrochloric acid until solution was complete. The solution was warmed to 45° at which point a green solid began to precipitate. After the mixture was heated at 45° for 1 hour, the solid was removed by filtration, washed with water and dried. The yield of dicarboximide **13** was 0.97 g. (87.5%).

B. Sodium Methoxide.—Tetraamide **12** (0.72 g., 0.0025 mole) was suspended in dry methanol (25 ml.) and sodium methoxide (0.27 g., 0.0050 mole) was added. The mixture was stirred at 25° for 2 hours during which time the yellow color was replaced by a brown color and ammonia was evolved. A solution of 10 ml. of 20% hydrochloric acid diluted to 150 ml. with water was added slowly. The green solid which precipitated was removed by filtration, washed with water and dried. The infrared spectrum showed it to be essentially pure **13**, 0.24 g. (38%).

Hydrolysis of Isothiazole 6.—Compound **6** (0.50 g., 0.0020 mole) was suspended in 10 ml. of concentrated hydrochloric acid. The flask was stoppered and the mixture was stirred at 25°. The suspension became deep orange in color within a few hours. After the mixture had been stirred for 2 days, the solid was collected by suction filtration, washed with water and dried. Recrystallization of the crude product (0.51 g.) from 50% ethanol gave 0.38 g. (67%) of copper-bronze plates, m.p. 215–225°. The infrared spectrum showed typical imide carbonyl absorption at 5.62 and 5.80 μ and amide carbonyl at 6.00 μ; amide bands occurred at 6.20 and 6.25 μ. There was no evidence of nitrile absorption in the spectrum. The ultraviolet spectrum in ethanol showed maxima at 374 (ϵ 4550), 275 (ϵ 12100) and 230 mμ (ϵ 18800).

Anal. Calcd. for $C_8H_3N_3O_3S_3$: C, 33.67; H, 1.06; N, 14.73; S, 33.72. Found: C, 33.44; H, 1.35; N, 14.99; S, 34.05.

Conversion of Dithiin 4 to Isothiazole 6 (Iodide Ion–Sulfur).—A mixture of **4** (2.0 g., 0.0093 mole), sodium iodide (2.0 g., 0.013 mole), sulfur (2.0 g., 0.063 mole) and iodine (0.1 g., 0.0004 mole) in DME (100 ml.) was stirred for 12 hours at 25°. Sulfur (1.4 g.) was removed by filtration and the filtrate was evaporated to dryness at room temperature. The residue was extracted with a small volume of warm benzene. The extracts were cooled and isothiazole **6**, 1.47 g. (59%), m.p. 179–181°, was deposited. The product was judged pure by its infrared spectrum.

^{13}C-Labeled Isothiazole 6.—Carbon disulfide (15.0 g., 0.20 mole) was added dropwise to a stirred suspension of commercial potassium cyanide-^{13}C (6.5 g., 0.10 mole, containing 65% ^{13}C) in DMF (50 ml.). The reaction was exothermic but the potassium (unlike sodium) salt remained in solution. Iodine (12.6 g., 0.10 mole) was added in small portions with stirring, and the mixture was then stirred overnight at 25°. The solvent was removed at room temperature and the residue was extracted with benzene. Evaporation of the benzene extract gave a solid which was chromatographed on neutral alumina. Elution with benzene gave a total of 300 mg. of labeled isothiazole **6**, m.p. 182°. The infrared spectrum was identical with that of an authentic sample.

The ^{13}C n.m.r. spectrum[22] was determined on a saturated tetrahydrofuran solution in a 3.8-mm. i.d. tube using a Varian 5-mm. probe insert and was measured at 8.5 Mc/s. under rapid passage dispersion mode conditions. The interpretation of the spectrum[22] is given in the body of this paper.

Thermal Conversion of Dithiin 4 to Isothiazole 6 with Sulfur.—Dithiin **4** (0.50 g., 0.0023 mole) and sulfur (1.5 g. 0.047 mole) were thoroughly mixed in a large test-tube which was then immersed in an oil-bath maintained at 200°. After 30 seconds the tube was withdrawn and cooled, and the black mass was extracted with carbon disulfide to remove sulfur. The residue was extracted with boiling benzene and the benzene extract was treated once with charcoal. On cooling, the benzene solution deposited 0.3 g. of **4**. By concentrating and cooling the filtrate, 0.09 g. (15%) of **6**, m.p. 165–175°, was isolated and identified by its infrared spectrum.

Disproportionation of 4. A. Urea Catalyst.—A mixture of **4** (0.50 g., 0.0023 mole), urea (10 mg.) and ethanol (50 ml.) was stirred overnight at 25° without apparent change. The solution was then heated under reflux for 2 hours, cooled and the solvent was evaporated at room temperature. The residue was extracted with boiling benzene, and cooling the extracts gave a solid product. Chromatography of the residue on neutral alumina gave a mixture of *ca.* 0.1 g. of **4** and 0.32 g. (56%) of **6**, m.p. 159–166°. The infrared spectrum showed that the isothiazole **6** obtained was only slightly impure.

B. Sodium Ethoxide Catalyst.—A mixture of **4** (2.16 g., 0.010 mole), 1 mmole of sodium hydride and 200 ml. of absolute ethanol was heated under reflux for 12 hours. The solvent was removed and fractional recrystallization of the residue from benzene gave approximately 0.01 g. (1%) of tetracyanothiophene, m.p. 197–198°, and 0.69 g. (27%) of **6** as yellow needles, m.p. 181–183°. Chromatography of the filtrates gave an additional 0.1 g. of **6**. Both products were identified by their infrared spectra.

Sodium Ethoxide Catalyst in the Presence of Sulfur.—A mixture of sodium hydride (0.024 g., 0.0010 mole), sulfur (0.40 g., 0.013 mole), and absolute ethanol (100 ml.) was heated under reflux for 15 minutes. The dark green-brown solution was stirred while **4** (2.16 g., 0.0010 mole) in ethanol (50 ml.) was added over 15 minutes. The first few drops of the dithiin solution gave a bright yellow coloration which gradually darkened to brown when the addition was complete. The mixture was heated at reflux for an additional 15 minutes and then cooled. Removal of the solvent and recrystallization of the residue from benzene gave 0.2 g. (9%) of recovered **4**, m.p. 210–213°, and 1.22 g. (55%) of **6**, m.p. 175–180°. Both products were characterized by their infrared spectra and no tetracyanothiophene was detected.

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Thiacyanocarbons. II. Chemistry of Disodium Dimercaptomaleonitrile

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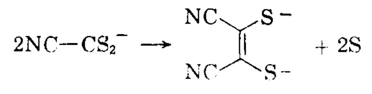
Sodium cyanodithioformate (1)[1] and disodium dimercaptomaleonitrile (3)[2] have proved to be valuable entries into the field of thiacyanocarbons, *i.e.*, cyanocarbons containing sulfur atoms. A study of the chemistry and stereochemistry of *cis*-3 and the new isomer, disodium dimercaptofumaronitrile, *trans*-16, was carried out. Physical and spectral studies of 3 and 16 and their derivatives are reported, and, remarkably, *cis*-3 is configurationally stable with respect to *trans*-16 and appears to be the isomer of greater thermodynamic stability. Weak bonding interaction of the *cis*-mercaptide groups in 3 is postulated to account for these findings. The equilibrium constant for the reaction bis-(methylmercapto)-fumaronitrile ⇌ bis-(methylmercapto)-maleonitrile was determined to be 3.23 at 25° ($\Delta H^{477} = -1.1 \pm 0.1$ kcal./mole, $\Delta S^{477} = -0.2 \pm 0.1$ e.u.). In the photochemical steady-state only the *cis* isomer of the pair exists. The photochemical steady-state ratio of the salts *cis*-3/*trans*-16 is 0.37.

Introduction.—In 1955, Bähr and Schleitzer[1] reported the synthesis of stable salts of the previously unknown cyanodithioformic acid ($NCCS_2H$) by reaction of alkali cyanides with carbon disulfide in dimethylformamide solution. Under certain conditions these salts dimerized spontaneously with loss of elemental sulfur to give the dianion of dimercaptomaleonitrile.[2]



The *cis* configuration was indicated by the large dipole moment (4.65 ± 0.08 D.) of the product of methylation, which was presumed to be bis-(methylmercapto)-maleonitrile.[3]

The highly unfavorable alignment of poles and dipoles proposed by Bähr for the dimerization product of the cyanodithioformate ion appeared unusual, and the present studies were undertaken in order to investigate the physical and chemical nature of "Bähr's salt." This paper discusses first some aspects of the chemistry of cyanodithioformic acid necessary as a preliminary to the following study of the chemistry of disodium dimercaptomaleonitrile.

The structure assignment of Bähr and Schleitzer has been confirmed and extended by the synthesis and isolation of the *trans* isomer, disodium dimercaptofumaronitrile. Selected methylation studies showed that each isomer yields a distinct dimethyl derivative in high yield, and dipole moment, infrared and ultraviolet spectral characterizations of these derivatives, given in the last section, are in accord with the stereochemical assignments that are employed throughout the text. The most convincing evidence for the assignments is based on the dipole moments of the methylation products, bis-(methylmercapto)-maleonitrile (μ = 5.08 D.) and bis-(methylmercapto)-fumaronitrile (μ = 1.57 D.). The latter isomer was reported by Bähr and Schleitzer[3] by another synthesis, but repetition of this synthesis showed that their product contained less than 10% of bis-(methylmercapto)-fumaronitrile (see discussion in footnote 5).

From thermodynamic studies it is concluded that the unusual stability of the *cis* isomers in this series of salts and methyl derivatives is a result of increased delocalization derived from contributing structures in which bonding between the sulfur atoms is significant.

Salts of Cyanodithioformic Acid.—Monomeric cyanodithioformic acid is unstable; however, sodium, potassium, a few heavy metal and tetraalkylammonium salts have been isolated.[1] These salts have been prepared from the sodium salt which was obtained by the addition of sodium cyanide to carbon disulfide in dimethylformamide (DMF) solution. The sodium salt **1**, when prepared in dimethylformamide, crystallized as a solvate containing three molecules of the solvent, and was stable to further chemical change in this medium.[1] The unsolvated tetraethylammonium salt **2** was obtained by treatment of the sodium salt with tetraethylammonium hydroxide in methanol, and heavy metal salts were prepared by similar metathetical reactions.[1]

In our work, the reaction of alkali cyanides with carbon disulfide was attempted in several of the usual organic solvents and in water. Only in amides (dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc.) was there evidence of reaction to give cyanodithioformate ion in significant yields. The effect of the cation was notable; sodium cyanide reacted quantitatively and exothermically, but potassium cyanide gave only low yields of cyanodithioformate ion with no heat evolution in dimethylformamide solution. When tetraethylammonium cyanide was employed in non-polar solvents, especially methylene chloride, the reaction with carbon disulfide was rapid and unsolvated tetraethylammonium cyanodithioformate was isolated directly in high yield. Cation type and solvent effects play a significant role in determining the rate of reaction of cyanide ion with

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[1] G. Bähr and G. Schleitzer, *Ber.*, **88**, 1771 (1955).

[2] G. Bähr, *Angew. Chem.*, **68**, 525 (1956); G. Bähr, G. Schleitzer and H. Bieling, *Chem. Tech.*, **8**, 596 (1956).

[3] G. Bähr and G. Schleitzer, *Ber.*, **90**, 438 (1957).