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.

[CONTRIBUTION NO. 756 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

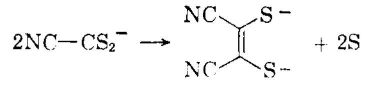
Thiacyanocarbons. II. Chemistry of Disodium Dimercaptomaleonitrile

BY HOWARD E. SIMMONS, DALE C. BLOMSTROM AND ROBERT D. VEST

RECEIVED MARCH 24, 1962

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 $\rightleftharpoons$ 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 ($\mu = 5.08$ D.) and bis-(methylmercapto)-fumaronitrile ($\mu = 1.57$ 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

---

[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).

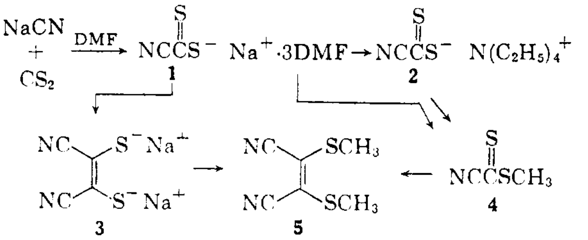
carbon disulfide, and these considerations are also important in the chemistry of the dianion of dimercaptomaleonitrile.

The salts of cyanodithioformic acid were investigated briefly. Tetraethylammonium cyanodithioformate (2) was stable in aprotic and amphiprotic media and showed no tendency to dimerize. The DMF-solvated sodium salt 1, however, dimerized with elimination of elemental sulfur in chloroform, carbon tetrachloride, methylene chloride and in water, the apparent rate being higher in the latter solvent. The product of the dimerization is disodium dimercaptomaleonitrile (3), a stable, crystalline solid.[2,4]

The thermal stabilities of 1 and 2 are very different. Heating the DMF-solvate of the sodium salt 1 under vacuum at 130° produced sulfur and disodium salt 3 in quantitative yield. None of the corresponding *trans* isomer was detected. On the other hand, the tetraethylammonium salt was stable in the molten state at 140–150° for 2 hours and was recovered unchanged.

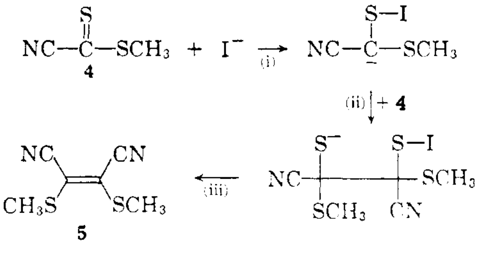
Methylation of tetraethylammonium salt 2 with methyl iodide in acetonitrile gave in 65% yield methyl cyanodithioformate (4), a stable, deep purple liquid. The reaction of sodium salt 1 with methyl iodide was difficult to control, since both dimethylformamide and iodide ion released in the reaction rapidly catalyzed the conversion 4 → 5 in this system (see below); however, in some runs low yields (*ca.* 25%) of the ester 4 could be isolated, which supports the view that cyanodithioformate anion is present in both the DMF complex 1 and the tetraethylammonium salt 2.

Ester 4 was converted to bis-(methylmercapto)-maleonitrile (5), m.p. 99°, with loss of elemental sulfur by treatment with catalytic amounts of anions (especially iodide and cyanide ion), by heating, and by ultraviolet irradiation. In the thermal experiments the *trans* isomer, bis-(methylmercapto)-fumaronitrile (13), m.p. 118–119°, was isolated in yields of less than 5%, and in the anion and light-catalyzed reactions none of the *trans* isomer was detected.[3,5]



The cyanodithioformate ion in salt 2 (lustrous, brown crystals) shows weak absorptions at 470 (ϵ 130) and 550 mμ (ϵ 16). The methyl ester 4 has a similar weak absorption at 530 mμ (ϵ 22). The nitrile stretching absorptions in 4, 1 and 2 occur at 4.52, 4.55 and 4.58 μ, respectively, and the carbonyl absorption in the DMF complex 1 is split into a doublet, 6.00 and 6.06 μ (pure DMF, 6.00 μ). This suggests that strong complexing of the cyanodithioformate ion with dimethylformamide occurs and promotes dimerization by reducing the negative charge on the anion. This seems reasonable since the covalent ester 4 is readily dimerized, while the free cyanodithioformate ion in 2 is stable in all solvents investigated.

The dimerizations (1 → 3) and (4 → 5) were not studied in detail but can be interpreted in the following manner, *e.g.*, 4 with iodide ion. Recently it was found[6] that electronegatively substituted thiocarbonyl compounds often undergo addition of nucleophiles (other than carbanions) in the inverse manner (i). The resulting stabilized carbanion attacks another molecule of ester at carbon (ii) to give an intermediate which corresponds to that expected in the oxidation of a 1,2-dimercaptide with iodine. Eventual sulfur loss to give the conjugated olefin (iii) would be the expected outcome of this sequence.[7]



The dimerization reaction is strongly influenced by the nature of the cation. When tetraethylammonium cyanodithioformate was treated with three moles of dimethylformamide and allowed to stand in chloroform, water, ethanol or acetonitrile, the solutions were stable and no dimerization occurred. These systems differed from that in which

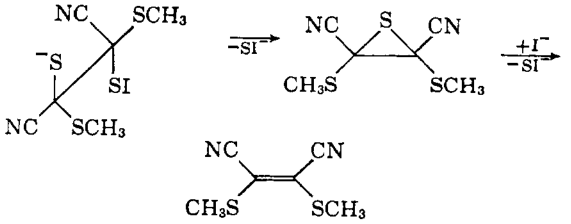
---

(4) No evidence for the formation of disodium dimercaptofumaronitrile could be obtained. The synthesis and characterization of the *trans* isomer are given below.

(5) Bähr and Schleitzer[3] treated salt 1 with methyl iodide in methanol and postulated the intermediate formation of 4 (not isolated) which they claimed dimerized spontaneously to bis-(methylmercapto)-fumaronitrile, m.p. 78°, μ = 3.86 ± 0.08 D. We repeated this experiment and found the product was largely *cis*-5, m.p. 99°, contaminated with a small amount (<10%) of *trans*-13, m.p. 118–119°. Presumably the high dipole moment found[3] was due to use of a sample rich in the *cis* isomer.

(6) W. J. Middleton, E. G. Howard and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961).

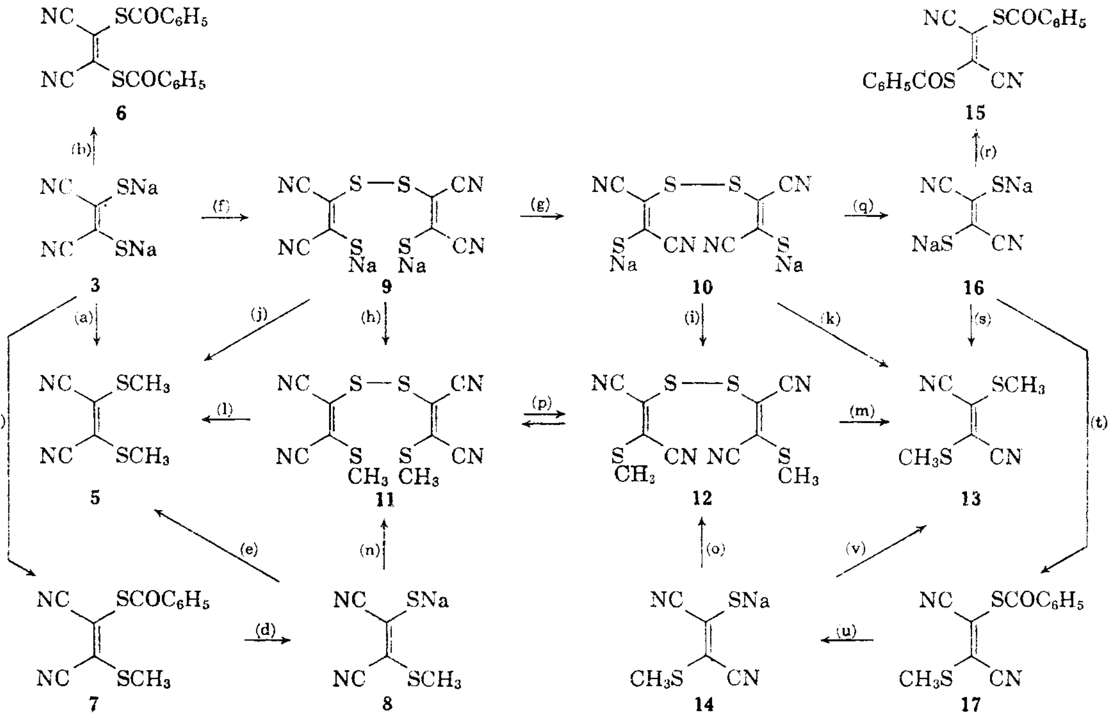
(7) That maleonitrile 5 is the predominantly formed isomer in i–iii can be rationalized if it is assumed that the product of reaction ii is the *threo* isomer. This assumption seems reasonable since addition of the bulky carbanion to the thiocarbonyl carbon should occur to minimize conformations which involve unfavorable steric and electrical repulsions. If in addition sulfur–sulfur bonding of the type proposed later in this paper is important in the transition state for the addition reaction, overlap of the (C–S⁻) and (C–SI) groups will also operate to favor formation of the *threo* isomer. Backside displacement of SI⁻ to give a thioepoxide followed by nucleophilic desulfurization is one reasonable path to the olefin. Nucleophilic desulfurization of thioepoxides by triphenylphosphine and anions, such as iodide ion, are known to be stereospecific, in that the configuration of the substituents remains unchanged in going from the thioepoxide to the olefin (see



D. B. Denny and M. J. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960)). It is further known that the maleonitrile 5 and fumaronitrile 13 are each configurationally stable in solution in the presence of iodide ion and iodine under the reaction conditions.

CHART I

CHEMISTRY OF DISODIUM DIMERCAPTOMALEONITRILE (3) AND DISODIUM DIMERCAPTO FUMARONITRILE (16)

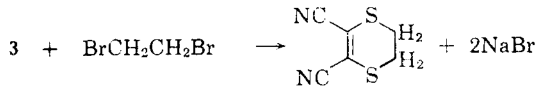


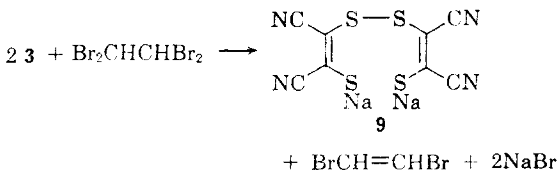
the sodium salt 1 readily lost sulfur solely by the replacement of sodium by tetraethylammonium ion.

Chemistry of Disodium Dimercaptomaleonitrile (3) and Disodium Dimercaptofumaronitrile (16).—The chemistry of disodium dimercaptomaleonitrile (3) is summarized in Chart I and will be discussed in the next four sections.

Disodium cis-**3** was methylated (a) in high yield with methyl iodide in water, methanol or 1,2-dimethoxyethane (DME) under various conditions to give pure cis-**5**, m.p. 99°, even when the methylation was carried out slowly in amphiprotic solvents. Similarly, dibenzoylation (b) with benzoyl chloride in DME gave a high yield of the pure *cis*-dibenzoyl derivative **6**, m.p. 121–123°. When salt **3** was treated successively with one mole of benzoyl chloride and one mole of methyl iodide (c), a homogeneous methyl benzoyl derivative **7**, m.p. 107.0–108.5°, was formed, which could be smoothly cleaved (d) at −20° with one mole of sodium methoxide in methanol to give the crystalline *cis*-monomethyl sodium salt **8**. Cleavage of the thioester was facile under these conditions and the methyl benzoate and solvent could be evaporated at −20°. Methylation of salt **8** with methyl iodide in methanol and in acetonitrile (e) gave high yields of pure *cis*-**5**.

cis-**3** is readily oxidized under mild conditions, and a more detailed study of the oxidation is given in a subsequent publication.[8] With one-half equivalent of oxidants such as bromine, iodine, thionyl chloride and tetracyanoethylene, salt **3** was converted (f) to disodium *cis-cis*-bis-(2-mercapto-1,2-dicyanovinyl) disulfide (**9**). The assigned structure of **9** will become evident in the following discussion. *cis-cis*-**9** is formed initially, but in certain polar solvents it is readily converted (g) to *trans-trans*-**10**, which is the only crystalline product usually isolated.[9] Although **3** undergoes simple displacement reactions with alkyl halides,[10] many polyhalogen compounds oxidize the salt. 1,2-Dibromoethane and **3** gave high yields of the metathetical product, 2,3-dicyano-5,6-dihydro-1,4-dithiin, but **3** underwent a clean oxidation reaction with 1,1,2,2-tetrabromoethane. When the latter reaction was carried out at 25° in DME solution, pure *cis-cis*-**9** was isolated in 31% yield after 3 minutes along with *cis*- and *trans*-1,2-dibromoethylene (49%) and sodium bromide. Yields increased with longer reaction times but contamination of the product by *trans-trans*-**10** became evident. After 2 hours, only *trans-trans*-**10** was isolated. When purified **9** was dissolved in DME, complete isomerization to **10** occurred in 2 hours. It is interest-





---

[8] Paper III in this series: H. E. Simmons, D. C. Blomstrom and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4772 (1962).

[9] G. Bähr, *Angew. Chem.*, **70**, 606 (1958), correctly inferred the gross structure of salt **9** obtained from the oxidation of **3** with iodine in water. The salt is depicted as having *cis–cis* geometry; however, repetition of this experiment has shown that the isolated salt is largely *trans-trans* **10** when the oxidation is carried out in methanol.

[10] German Patents 1,060,655 (1957) and 1,077,915 (1958), assigned to E. Merck. Other examples will be found in the present series of papers.

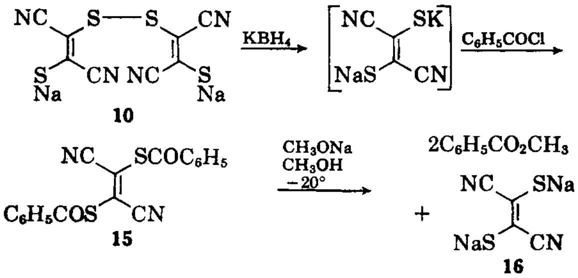
ing and significant that salt **9** is stable to further oxidation by 1,1,2,2-tetrabromoethane which thus far is the only selective oxidant found that cleanly oxidizes salt **3** but is inert to salts **9** and **10**. The mechanism of this oxidation will be discussed in a later publication.

The structures of salts **9** and **10** were determined by reductive cleavage to two moles of the salts **3** and **16**. Disodium *cis-cis*-**9** was cleaved with potassium borohydride in methanol–tetrahydrofuran and the fragments were methylated in 58% yield. The product was pure *cis*-**5** and no *trans*-**13** could be detected spectrally. Similarly, *trans-trans*-**10** was cleaved in DME and subsequent methylation gave an 83% yield of a mixture of *trans*-**13** and *cis*-**5** in the ratio 1.91:1. It will be shown below that isomerization to give *cis*-**5** in the latter reduction is to be expected on the basis of the studies in Table I.

Salts **9** and **10** gave the corresponding dimethyl derivatives as crystalline solids, **11**, m.p. 102–104°, and **12**, m.p. 123–126°, respectively (h, i), when the methylations were carried out with dimethyl sulfate at 25° on freshly prepared solutions.

The configurational stability of salts **3**, **8**, **9**, **10**, **14** and **16** will be seen to be a function of the reaction variables. Alkylation and acylation of these salts and certain reductive cleavage reactions of **9**, **10**, **11** and **12** are dependent on these factors and throw light on the equilibria involved with the various mono- and dianions. The synthetic aspects of Chart I will be completed without proof before considering the questions of stereochemistry which have allowed the assignments in Chart I to be made.

The *trans* isomer **16** corresponding to salt **3** was synthesized by the following route. Salt **10** was reduced smoothly with potassium borohydride (q) and the crude reduction product was treated rapidly with benzoyl chloride at low temperature (r). Purified *trans*-dibenzoyl derivative **15**, m.p. 144–150°, was cleaved with sodium methoxide in methanol at −20° and crystalline disodium dimercaptofumaronitrile (**16**) was isolated. Methylation of salt **16** with methyl iodide (s) in aqueous acetone gave a high yield of *trans*-**13**, m.p. 118–119°, which was of > 95% purity.



trans-**16**, as the bis-(tetramethylammonium) salt, was also converted to *trans*-methyl benzoyl derivative **17**, m.p. 74.5–75.5°, and to *trans*-monomethyl sodium salt **14** by a sequence of reactions (t, u) similar to those employed in the *cis* series (c, d). That the configuration of salt **14** is correct was shown by its conversion under certain conditions (v) to *trans*-**13**. Other reactions in the *trans* series that are complementary to those discussed above for the *cis* series are recorded in the Experimental Section but are not discussed in detail here.

Stereochemistry of Salts 3 and 16.—The configurational stability of certain mono- and dianions presented in Chart I has been found to be dependent on the nature of the associated cation (metal or tetraalkylammonium) and of the solvent. Methylation of salts **9**, **14** and **16** for example, gave results which were highly dependent on these factors. Similarly, reductive cleavage of disulfides **9**, **10**, **11** and **12** followed by methylation gave results that at first sight appeared conflicting. The influence of solvent and cation on the geometrical integrity and stability to chemical change of the various anions is outlined in Table I. These observations will not be discussed in detail, but some general conclusions are evident.

TABLE I

INFLUENCE OF SOLVENT AND CATION ON THIACYANOCARBON ANION STABILITY

Anion of[h]	Cation	Solvent and conditions	Recovery, %[a]	*cis*: *trans*[b]
3	Na^+	H_2O, 17 hr., 100°	100	100:0
		C_2H_5OH, 3 hr., 70°	100	100:0
		CH_3CN, 42 hr., 25°	63	100:0
	$(CH_3)_4N^+$	H_2O, 63 hr., 110°	11	100:0
		CH_3OH, 48 hr., 25°	55	100:0
		CH_3CN, 42 hr., 25°	22	75:25
16	Na^+	H_2O, 17 hr., 100°	100	0:100
		C_2H_5OH, 2 hr., 25°	100	0:100
		C_2H_5OH, 3 hr., 70°	65	0:100
		C_2H_5OH, 4 hr., 70°[c]	65	50:50
		CH_3CN, 42 hr., 25°	32	0:100
		DME, 48 hr., 25°	[d]	[d]
	$(CH_3)_4N^+$	H_2O, 19 hr., 75°	100	0:100
		H_2O, 63 hr., 110°[g]	74	26:74
		CH_3OH, 72 hr., 25°[e]	100	0:100
		CH_3CN, 42 hr., 25°	[d]	[d]
8	Na^+	H_2O/CH_3OH, 15 min., 25°	100	100:0
		C_2H_5OH, 2 hr., 78°	100	100:0
		C_2H_5OH + KI, 2 hr., 78°	100	100:0
		CH_3CN, 2 hr., 82°	100	100:0
14	Na^+	C_2H_5OH, 0.5 hr., 25°	100	70:30
		C_2H_5OH, 1 hr., 78°	100	100:0
	$(CH_3)_4N$[e]	H_2O, 48 hr., 25°	100	0:100
		C_2H_5OH, 6 hr., 25°	100	5:95
		C_2H_5OH, 24 hr., 25°	100	10:90
9	Na^+	H_2O, 24 hr., 25°	100	[f]
		C_2H_5OH, 24 hr., 25°	100	[f]
		DME, 2 hr., 25°	100	95% **10**
10	Na^+	H_2O, 24 hr., 25°	100	100% **10**
		C_2H_5OH, 24 hr., 25°	100	100% **10**
		DME, 24 hr., 25°	100	100% **10**

[a] Solutions were dilute (*ca.* 0.01 *M*) and, in general, oxygen-free. In several cases the presence of oxygen was shown to have no effect on the results. Stabilities were studied by following changes in the ultraviolet spectrum and then analyzing spectrally the methylation products. No attempt was made to determine optimum conditions of stability or precise equilibrium constants. The details are given in the Experimental Section. [b] Both isomers were determined as in a. [c] Run in presence of KBH_4 to suppress air oxidation. [d] Extensive decomposition, recovered no **3** or **16**. [e] In some runs decomposition occurred accompanied by formation in 50% yield of *trans-trans*-**10**. [f] Largely isomerized to trans-trans-**10**, but not accurately determined. [g] Run in the dark. [h] See Chart I for formulas.

The configurational stability of *cis*-**3** or *cis*-**8** was largely independent of solvent and cation. Disodium *trans*-**16** was stable in polar, amphiprotic solvents, such as water, but isomerization to *cis*-**3** accompanied by extensive decomposition occurred in less polar solvents, such as ethanol and especially aprotic solvents like acetonitrile and DME. With non-coördinating cations, *e.g.*, [$(CH_3)_4N^+$], *trans*-**16** slowly isomerized to the *cis* isomer in water and underwent complete decomposition in less polar solvents. Bis-(tetramethylammonium) *cis*-**3** was configurationally and chemically stable in water, and it is important to note that, although this salt slowly decomposed in acetonitrile, it could be partially recovered (22%) after 2 days as a mixture of *cis* and *trans* salts in the ratio 3:1. Tetramethylammonium *trans*-**14** was configurationally stable with respect to *cis*-**8** in polar solvents, but even weakly coördinating cations (Na^+) were effective in bringing about isomerization in ethanol.

The results of methylation and reductive cleavage studies of the various salts can now be understood in terms of the observations in Table I. The methylations described below were usually high-yield reactions (>85%). *cis*-**3** (Na^+ and $(CH_3)_4N^+$) gave only *cis*-**5** when methylated with methyl iodide in water, methanol, ethanol, acetonitrile and DME, regardless of the order or rate of addition of the reagents. Methylation of disodium *trans*-**16** in methanol with methyl iodide, when the reagents were mixed in one operation, gave *cis*-**5** and *trans*-**13** in the ratio 1:4. When the methyl iodide was added over 30 minutes the ratio was 7:3. When an aqueous solution of the salt was added to an aqueous acetone or methanol solution of methyl iodide over 30 seconds the ratio was 1:19. Presumably isomerization in these reactions occurred at the stage of half methylation, since according to Table I *trans*-**14** is much more rapidly isomerized than *trans*-**16** under the conditions cited.

Sodium *trans*-**14** and methyl iodide gave approximately 40% *trans*-**13** and 60% *cis*-**5** when the reagents were mixed in one operation in methanol. Under the same conditions tetramethylammonium *trans*-**14** gave pure *trans*-**13**. It is evident that the sodium ion facilitated isomerization from the *trans* to the *cis* isomer in the monoanion series. This conclusion was further supported by allowing a methanol solution of tetramethylammonium *trans*-**14** to stand for 6 hours at 25°. Methylation of one-half of the solution gave **5** and **13** in the ratio 1:19, and after 24 hours methylation of the other half of the solution showed only a modest increase of the **5**:**13** ratio to 1:9. A similar reaction with the corresponding sodium salt gave largely the *cis* isomer **5**.

Stereochemistry of Disulfides 9, 10, 11 and 12.—As mentioned above, *cis-cis*-**9** and *trans-trans*-**10** gave homogeneous dimethyl derivatives when treated with methyl sulfate in ice-water (h, i). The crystalline derivatives **11** and **12** were also synthesized by oxidative coupling of the monomethyl salts **8** and **14**, and these reactions clearly establish the presence of a disulfide bond.

When sodium *cis*-**8** was oxidized with potassium ferricyanide in water pure *cis-cis*-**11** was obtained in 76% yield (n). Under similar conditions *trans*-**14** gave almost pure *trans-trans*-**12** in good yield (o). Other oxidation systems gave less clear-cut results and mixtures were obtained. Sodium *cis*-**8** and thionyl chloride in DME gave a good yield of a mixture of *cis-cis*-**11** and *trans-trans*-**12** in the ratio 55:45. Nothing is known concerning the mechanism of any of these reactions and the high degree of stereospecificity in the former oxidation and of isomerization in the latter is not fully understood. It may be that oxidation in aqueous solution gave *cis-cis*-**11** stereospecifically, and in the aqueous system the insoluble disulfide precipitated immediately. The *cis-trans*-disulfide corresponding to **11** and **12** was not detected with certainty in these reactions, and its preparation and characterization are described below.

Although methylation of *cis-cis*-**9** and *trans-trans*-**10** gave the expected metathetical products with methyl sulfate (h, i), methylation of disodium **9** and **10** with methyl iodide in various solvents gave good yields of the cleavage products **5** and **13** (j, k). Thus, *trans-trans*-**10** in DME gave an 86% yield of a mixture of *trans*-**13** (>93%) and *cis*-**5** (<7%), based on infrared spectral analysis; *cis-cis*-**9** gave 90% *cis*-**5** and 10% *trans*-**13**. The unexpected difference in methylations with methyl sulfate (h, i) and methyl iodide (j, k) is readily explained by reductive cleavage of the initially formed methyl derivatives **11** and **12** by iodide ion liberated in the latter methylations.

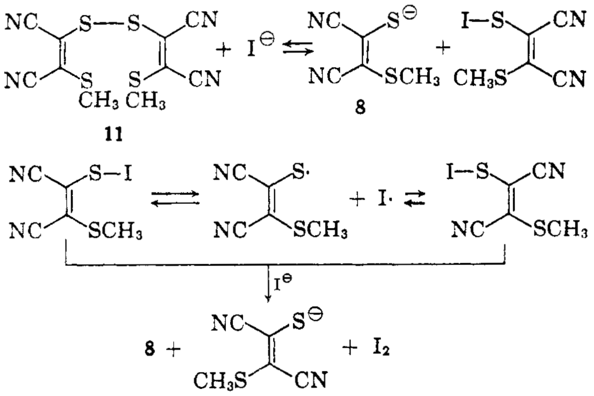
The above conclusion was confirmed by treating *cis-cis*-**11** and *trans-trans*-**12** with two moles of sodium iodide in DME solution. Iodine was liberated almost quantitatively, and subsequent methylation with methyl iodide gave mixtures of *cis*-**5** and *trans*-**13** in good yields (l, m). In reactions l and m, the ratios of **5**:**13** were 5.7:1 and 3.4:1, respectively. Based on the observations in Table I, it would be expected that methylation following reductive cleavage of *cis-cis*-**11**, which forms *cis*-**8**, and of *trans-trans*-**12**, which forms *trans*-**14**, would result in exclusive formation of *cis*-**5** in the former case and a mixture of *cis*-**5** and *trans*-**13** (predominating) in the latter. Since mixtures of **5** and **13** were formed in *both* reactions, a further factor leading to configurational instability must be sought in the iodide ion cleavages.

Since **11** and **12** were readily cleaved by stoichiometric amounts of iodide ion, it was not surprising to find that catalytic amounts of iodide ion caused the interconversion of *cis-cis*-**11** and *trans-trans*-**12**. In 45 minutes at 25°, solutions of both **11** and **12** in DME were converted to the equilibrium mixture which contained approximately 60% *cis-cis*-**11** and 40% *trans-trans*-**12** (p).[11] The isomerization which occurred during the cleavage reactions employing molar quantities of potassium iodide may thus only reflect the instability of the pure isomers to iodide ion *before* cleavage.

The familiar equilibrium involved in the oxidation of mercaptide ion by iodine to give disulfides lies far to the left with these electronegatively substituted disulfides, and **11** and **12** resemble peroxides rather than disulfides. The isomerization observed in the fragments from the cleavage reactions employing a full equivalent of iodide ion (and similarly the catalyzed interconversion of **11** and **12**) can be formulated in the following manner in the case of

---

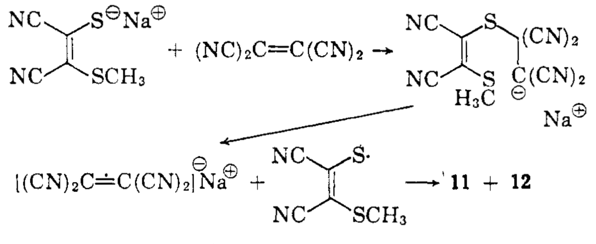
(11) The preparation and characterization of the third possible isomer, *cis-trans*-bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide, is described in the next section. The difficulty of detecting with certainty the *cis-trans* isomer in mixtures causes the above ratio to be accepted with reserve. It is presumed that the *cis-trans* isomer was present on mechanistic grounds in the products of the iodide ion-catalyzed isomerization of *cis-cis*-**11** and *trans-trans*-**12** and in certain oxidations of **8** and **14** described above and below.



11 **8** **14**

cis-cis-**11**. Direct displacement by iodide ion at disulfide sulfur[12] in **11** gives **8** (stable) and an unstable sulfenyl iodide, which can undergo reaction with iodide ion to give iodine and a second molecule of **8**. It is postulated that the sulfenyl iodide is dissociated in the configurationally unstable radical $\cdot S(CN)C{=}C(CN)SCH_3$, so that reduction ultimately gives a mixture of **8** and **14**.[11]

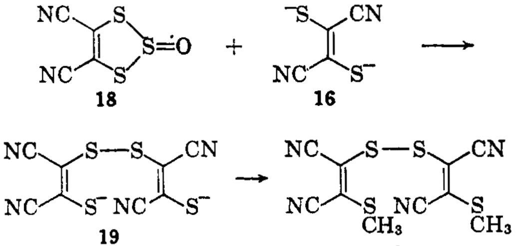
Evidence that the monoradical may be unstable was provided by the oxidation of disodium *cis*-**8** with tetracyanoethylene, a known one-electron oxidant. In tetrahydrofuran there was obtained an 81% yield of a mixture of *cis-cis*-**11** and *trans-trans*-**12** in the ratio 2:1.[11] Sodium tetracyanoethylenide was also formed in high yield, and the reaction is thought to proceed as shown. A similar oxidation of disodium *cis*-**3** with tetracyanoethylene to give *cis-cis*-**9** is reported in paper III.[8]



The reductive cleavage of *trans-trans*-**12** was also studied using potassium borohydride and sodium dithionite. The reductions were very rapid and in each case methyl iodide was added approximately 5 minutes after reduction; the product mixtures of **5** and **13** were then analyzed by their infrared spectra. The products depended strongly on both the reducing agent and the polarity of the reaction media. The following results were observed: potassium borohydride in DME gave **5** and **13** in the ratio 1:1.9; potassium borohydride in tetrahydrofuran–methanol, 1:0.6; sodium dithionite in aqueous methanol, 1:7.6. The reductive cleavage of *cis-cis*-**11** by potassium borohydride in DME and by sodium dithionite in aqueous methanol gave 85 and 78% yields, respectively, of essentially pure *cis*-**5** after methylation.

Thermal Isomerization of *cis-cis*-11 and *trans-trans*-12.—In the isomerizations of **11** and **12** and in the oxidation reactions of **8** and **14**, the third possible isomer, *cis-trans*-bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide, could not be detected with certainty (see below), although in some reactions, especially the oxidations of **8** and **14** by tetracyanoethylene and thionyl chloride, this isomer probably was formed.

The synthesis of the *cis-trans* isomer **20** was accomplished by the following route. Dicyano-1,2,3-trithiole-2-oxide (**18**)[13] has been shown in paper III[8] of this series to react with *cis*-**3** to give *cis-cis*-**9** in a stereospecific ring-opening reaction. Similarly, *trans*-**16** was treated with the trithiole oxide **18** and immediate methylation of the reaction mixture gave the desired *cis-trans*-dimethyl derivative **20** in good yield as an oil which could not be caused to crystallize. The reaction presumably proceeded *via cis-trans*-**19**. It was further determined that synthetic mixtures of *cis-cis*-**11** and *trans-trans*-**12** were oils that could be readily seeded with the pure isomers to give good recovery of the components. *cis-trans*-**20** synthesized above could not be induced to deposit either **11** or **12** on repeated attempts at seeding. All three isomers were unstable to attempted chromatographic separation.



18 **16** **19** **20**

The ultraviolet spectra of the *cis-cis*, *trans-trans* and *cis-trans* isomers were very similar so that synthetic mixtures could not be analyzed by this method. *cis-cis*-**11** showed a single, well resolved band at 340 mμ, the extinction coefficient diminishing rapidly toward longer wave lengths. *trans-trans*-**12** showed two bands in this region at 342 and 368 mμ. *cis-trans*-**20** had a single absorption (see Table II) at 350 mμ. A synthetic 1:1 mixture of *cis-cis*-**11** and *trans-trans*-**12** had a spectrum similar to, but distinguishable from, that of *cis-trans*-**20**. All spectra were recorded in methylene chloride.

cis-cis-**11** and *trans-trans*-**12** are most clearly distinguished in the infrared spectrum by bands at 8.56 and 11.82 μ (**11**) and 8.72 and 12.28 μ (**12**); otherwise the spectra were very similar. The spectrum of *cis-trans*-**20** showed essentially all of the bands present in both **11** and **12**, and the three isomers could only be distinguished on the basis of intensity relationships. The spectrum of the *cis-trans* isomer was very similar to that of a 1:1 mixture of **11** and **12**; however, the synthetic 1:1 mixture could be separated by fractional crystallization.

It was found that although both **11** and **12** could be recrystallized without change at low temperatures (<25°), brief heating of either isomer in carbon tetrachloride caused their interconversion, as

---

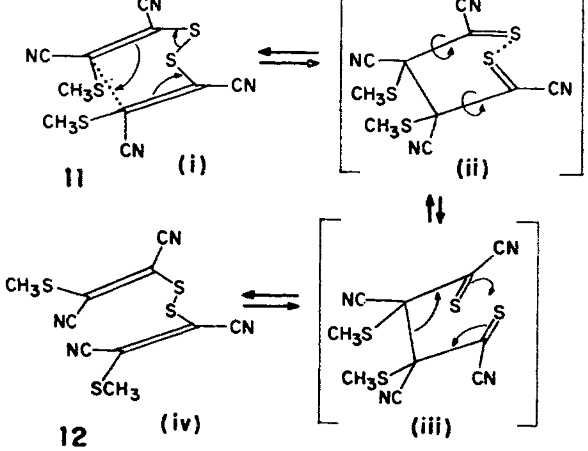
[12] See O. Foss in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p. 83, for examples of nucleophilic attack at disulfide bonds.

[13] H. E. Simmons, D. C. Blomstrom, R. D. Vest, J. R. Roland and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962); also see G. Bähr, *Angew. Chem.*, **70**, 606 (1958).

did prolonged heating in the melt. The infrared spectra of the mixtures obtained from the solution and melt equilibrations were identical and indicated a ratio of **11** to **12** of approximately 2:1. *trans-trans*-**12** could be separated readily by fractional crystallization from the products of these experiments. The spectra of the initially formed mixture did not indicate the presence of *cis-trans*-**20**.

It was further found that after heating *cis-trans*-**20** under conditions that gave equilibration of **11** and **12**, the spectrum was completely unchanged; *i.e.*, the intensity relationships in *cis-trans*-**20** after thermal treatment were *unchanged* but were different from those of the equilibrium mixture derived from either **11** or **12**. Thus, the *cis-cis* and *trans-trans* isomers are thermally interconvertible but the *cis-trans* isomer is stable under the same conditions.

Such a conclusion places stringent requirements on the mechanism of isomerization. The possibility of thermal dissociation of **11**, **12** and **20** into configurationally unstable free radicals (see above) must be ruled out, and the interconversion of **11** and **12** must proceed *via* a path which forbids the formation of the unsymmetrical isomer. Although this process has not been studied in detail, an intriguing possibility exists to account for these observations. The following outline presents the salient points for the interconversion *cis-cis*-**11** ⇄ *trans-trans*-**12**, which can be interpreted conceptually as a Cope rearrangement. Scale molecular models show that the β- and β'-carbons in the vinyl groups can lie over each other in the direction of maximum π-overlap (dotted line) in a configuration of minimum non-bonded repulsions only when the disulfide linkage assumes its usual[14] conformation and when the methylmercapto and cyano groups are staggered (for steric reasons) as shown in i. Synchronous bond-making and opening of the disulfide linkage (i) gives a bis-(thiocarbonyl) intermediate whose cyano and methylmercapto groups are fixed in a *trans* configuration (ii). The key consideration is that reformation of the disulfide bond is a specific process in geometrical terms. The thiocarbonyl sulfur atoms have their maximum electron density only above and below the plane of the bond, so that recombination ii → i must be highly directional (unlike the approach of two atoms whose charge densities are spherical). However, single bond rotation as shown in ii can lead to the mirror image structure iii, and this is presumably the only other conformer which meets the geometrical requirement of maximum overlap for reforming the disulfide bond. The result of iii → iv is the reformation of π-bonds about which the cyano groups are oriented *trans*. Furthermore, this process requires the simultaneous shifting of the configuration about *both* double bonds so that *cis-cis*-**11** can give only *trans-trans*-**12**, and *vice versa*.

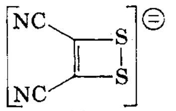


When this mechanism is applied to the *cis-trans* isomer **20**, it is seen that since both vinyl groups are required to invert their configurations simultaneously, the *cis-trans* isomer can only be converted into itself, which is in accord with the experimental observations.

Electronic Structure of Salts 3 and 16.—The chemistry of disodium dimercaptomaleonitrile (**3**) and its derivatives discussed in the previous sections has clearly pointed out the unexpected stereochemical stability of several molecules containing the dimercaptomaleonitrile group. In this section, some considerations which bear on the electronic structure of these molecules are summarized. Initially, two possibilities were considered to account for the stereochemical stability of *cis*-**3**.

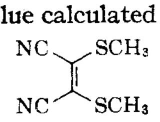
(1) Salts **3** and **16** are best represented by the classical (resonance-stabilized) mercaptide structures. The unfavorable electrical consequences of the alignment of poles and dipoles in the *cis* isomer are largely overcome by the high coördination energy of the *cis*-1,2-dimercaptide structure even with alkali metal cations.[15] Strong hydrogen bonding in amphiprotic solvents may even be sufficient to lower the energy of *cis*-**3** relative to that of *trans*-**16**.

(2) Salt **3** is best represented by a cyclic structure **21**. Stability is attributed to increased delocalization resulting from covalent bonding between the sulfur atoms. The reason for the introduction of this apparently complicating suggestion and the precise formulation of **21** will be discussed below.



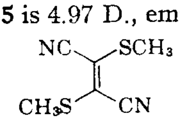
21

The *cis*, *trans* assignments of **5** and **13**, the respective methylation products of salts **3** and **16**, are based on their dipole moments in benzene. The value calculated for *cis*-**5** is 4.97 D., employing group moments for the aromatic series.[16] If bond-



$$(NC)_2C{=}C(SCH_3)_2$$

5, $\mu = 5.08$ D.



$$NC(CH_3S)C{=}C(SCH_3)CN$$

13, $\mu = 1.57$ D.

---

[14] See J. Donohue in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, p. 1.

[15] Strong complexes of the *cis* dianion **3** with heavy metal ions, such as palladium, copper and nickel, have been reported in ref. 2 and 13.

[16] L. E. Sutton in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Eds., Academic Press, Inc., New York, N. Y., 1955, p. 373.

ing interaction between the sulfur atoms is significant in *cis*-**5**, presumably rotation of the methylmercapto groups would be restricted, but observed dipole moments give no information concerning this point.[17] Such a structure would also possess a dipole moment of the order of 5 D., and the conclusion that the isomer m.p. 99° is the *cis* isomer is not altered. The measured moment of pure *trans*-**13** is 1.57 D., which is in disagreement with the high value reported by Bähr.[3,5] Of the three possible planar conformers of *trans*-**13**, two have zero dipole moment and one a value of 1.80 D. Appreciable moments for symmetrical *trans* isomers[18] and 1,4-disubstituted benzenes[17] are well known and may arise from restricted rotation. These results can accommodate the assigned structures within the limits of our knowledge of the degree of free rotation in these systems.

trans-**13** shows no absorption in the double bond stretching region in the infrared spectrum, as expected, and *cis*-**5** has a strong band at 6.70 μ which has been assigned to this vibration. 2,3-Dicyano-5,6-dihydro-1,4-dithiin absorbs at 6.65 μ, and all simple alkylated derivatives of *cis*-**3** have a strong band in the range 6.60–6.70 μ. The large shift to long wave length of the (C=C) stretching vibration is not unexpected in an ethylene symmetrically substituted simultaneously with strongly conjugated electron-withdrawing and -attracting groups. The absorptions in the 6–7 μ region of **3**, **5**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **16** and **20** are given in Table II.

The single absorption at 6.70 μ in the (C=C) stretching region of the covalent derivative **5** is displaced to 6.95 (Na^+) and 7.17 μ [$(CH_3)_4N^+$] in the *cis* dianion **3**. The 6–7 μ region is expectedly blank in the sodium and tetramethylammonium salts of the corresponding *trans*-**16**. The double bond absorptions appear at 6.83–7.04 μ in the various salts of the dianions **9** and **10**, none of which possess symmetrically substituted double bonds. In *trans-trans*-**10**, there is no opportunity for sulfur–sulfur interaction of the type considered above, although such interaction in *cis-cis*-**9** is still conceivable. The fact that *trans-trans*-**10** and *cis*-**3** absorb at virtually the same wave length, 6.97 and 6.95 μ, respectively, indicates that their bond orders are similar, and this would imply that the carbon–carbon double bond in *cis*-**3** approximates closely to that expected of the open dimercaptide structure for **3**. The shift of the (C=C) stretching vibration to longer wave length in *cis*-**3** when sodium ion is replaced by tetramethylammonium ion is probably associated with the strong coördinating ability of the *cis* dianion with even weakly chelating cations such as sodium ion. This effect is not evident in the monoanion series.

The ultraviolet spectra of the various derivatives are also recorded in Table II. It is seen that the *trans* isomers in the covalent and dianion salt series absorb at longer wave length than the corresponding *cis* isomers. Disodium *trans*-**16** absorbs at 44 mμ longer wave length than disodium *cis*-**3**. Significantly, disodium *trans-trans*-**10** absorbs at 40 mμ longer wave length than disodium *cis-cis*-**9**. If any special stabilization exists in *cis*-**3** because of sulfur–sulfur interaction, it does not seem to be reflected in the spectra, unless it is assumed that the electronic environment in each half of *cis-cis*-**9** is very similar to that in *cis*-**3**. This effect is absent in the monoanions. Sodium *cis*-**8** absorbs at 370 mμ (ethanol), while sodium and tetramethylammonium *trans*-**14** absorb at 369 mμ (methanol) and 373 mμ (ethanol), respectively. It is interesting to note that diphenylfumaronitrile and diphenylmaleonitrile show λ_{max} 339 mμ (log ε 4.37) and 399.5 mμ (log ε 2.94), respectively.[17] An inverse effect is noted in the thiacyanocarbon series in both λ_{max} and log ε. Bis-(methylmercapto)-fumaronitrile (**13**) has λ_{max} 364 mμ (log ε 4.01) and bis-(methylmercapto)-maleonitrile (**5**), λ_{max} 340 mμ (log ε 4.11). The shift of the high intensity, long wave length band to higher energy on going to the maleonitrile, in which coulombic repulsions would have been expected to lower the energy of transition to the first excited state, suggests some new electronic factor is operative in the *cis* isomer. It will be seen below that the ground state (thermodynamic) energy of the maleonitrile is lower than that of the fumaronitrile.

TABLE II

SPECTRAL DATA FOR THIACYANOCARBON DERIVATIVES

Compound[e]	Cation	(C=C)str., μ	λ_{max}, mμ (ε)
5		6.70[a]	272 (4,420), C_2H_5OH 340 (12,900)
13		..[a,d]	364 (10,300), C_2H_5OH
3	Na^+ $(CH_3)_4N^+$	6.95[a] 7.17[b]	368 (11,400), C_2H_5OH 372 (12,000), CH_3OH 366,[c] H_2O
16	Na^+ $(CH_3)_4N^+$	..[a,d] ..[b,d]	412 (10,100), C_2H_5OH 402 (10,200), H_2O 409 (12,900), CH_3OH
8	Na^+	6.80[a]	270 (4,950), C_2H_5OH 370 (13,900)
14	Na^+ $(CH_3)_4N^+$	7.06[b] 7.00[b]	369,[c] CH_3OH 373 (11,800), C_2H_5OH
9	Na^+ $(CH_3)_4N^+$	6.85,[a] 6.87[b] 6.83[a]	392 (16,000), C_2H_5OH 250 (12,900), C_2H_5OH 382 (19,400)
10	Na^+ $(CH_3)_4N^+$	6.98,[a] 6.97[b] 7.04[b]	432 (16,700), C_2H_5OH 374 (16,400), C_2H_5OH 433 (19,100)
11		6.68[a]	345 (17,680), C_2H_5OH 340,[c] CH_2Cl_2
12		6.67[a]	340 (13,700), C_2H_5OH 368 (16,950) 342,[c] CH_2Cl_2 368[c]
20		6.65	350,[c] CH_2Cl_2 345 (17,700), C_2H_5OH

[a] Run in KBr pellets. [b] Run in Nujol. [c] Intensity not determined. [d] Bands in this region absent from spectrum. [e] See Chart I for formulas.

The polarographic half-peak potentials for oxidation of disodium *cis*-**3**, *trans*-**16** and *trans-trans*-**10** were determined as described in the Experimental Section. Both *cis*-**3** and *trans*-**16** showed two well-defined waves in aqueous solutions containing various added electrolytes. The half-

---

[17] *Cf.* hydroquinone dimethyl ether, discussed in G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 239.

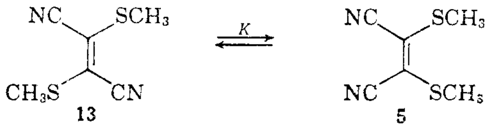
[18] A. J. Williams and R. J. W. Le Fèvre, *J. Chem. Soc.*, 2425 (1957), found the dipole moments of diphenylmaleonitrile and diphenylfumaronitrile were 5.7 and 1.1 D., respectively.

peak potentials were almost indistinguishable for both isomers: *cis*-**3**, $E_{p/2}$ = +0.08 and +0.40 v.; *trans*-**16**, $E_{p/2}$ = 0.00 and +0.43 v. *trans-trans*-**10** showed only a single peak at all concentrations studied ($E_{p/2}$ = 0.40 v.), which corresponds well with the second wave of **3** and **16**, both of which are known to give the disulfide salt on one-electron oxidation. The fact that the first waves of **3** and **16** occur at almost equal potentials suggests that the first ionization potentials of the *cis* and *trans* isomers are also similar. It might be expected that the close proximity of the two formal negative charges in the open dimercaptide structure for *cis*-**3** would lower the first ionization potential with respect to *trans*-**16**. The fact that the energy of the electron which is removed from *cis*-**3** on oxidation appears to be lower than expected may indicate that some special electronic stabilization exists in the *cis* isomer, or it may only mean that charge dispersal by classical delocalization effects is large in both isomers. The polarographic data are discussed further in paper IV of this series.

It was hoped that a study of equilibria such as **3** ⇄ **16** and **5** ⇄ **13** would shed some light on the question of the ground state energies of the *cis* and *trans* isomers. Little information is available on the stabilities of substituted maleo- and fumaronitriles; however, the status of the diphenyl derivatives has recently been clarified. Diphenylmaleonitrile, m.p. 243°, and diphenylfumaronitrile, m.p. 161°, have received unequivocal assignments as a result of X-ray studies on the *trans* isomer by Timmons and Wallwork.[19] These assignments are in agreement with the dipole moment studies of Williams and Le Fèvre[18] and represent an example of a *cis* isomer having a higher melting point than the corresponding *trans* isomer.[20] These authors[18] also found that diphenylfumaronitrile is rapidly isomerized by sunlight and ultraviolet light to diphenylmaleonitrile, which is stable to dark storage. It is not known which isomer has the lower energy in the thermodynamic sense, but the literature reveals an interesting observation that bears on this point. Knoevenagel and Bergdolt[21] observed that diphenylsuccinonitrile was dehydrogenated over a palladium catalyst at 250° to give approximately 20% diphenylfumaronitrile, m.p. 158°, along with cleavage products such as phenylacetonitrile. None of the high melting *cis* isomer was detected. Since it is well known that noble metal catalysts accelerate the attainment of thermodynamic equilibrium between *cis* and *trans* isomers, it can be inferred that diphenylfumaronitrile is of lower energy than diphenylmaleonitrile, as expected on steric and electrical grounds.

It is also known that dichloromaleonitrile is converted to dichlorofumaronitrile[22] by heat and probably by anions.[23,24]

Bis-(methylmercapto)-maleonitrile (**5**) and bis-(methylmercapto)-fumaronitrile (**13**) were equilibrated thermally in the melt. The equilibrations were carried out in the presence of a catalytic quantity of iodine in Pyrex tubes in the dark under a nitrogen atmosphere. Each isomer gave the identical mixture in the times indicated, and the results were unchanged in one run when the experiment was repeated in the absence of iodine. The equilibrium constant, $K = [cis\text{-}\mathbf{5}]/[trans\text{-}\mathbf{13}]$, was determined spectrophotometrically on the reaction mixtures. It can be estimated that K = 3.23 at 25°, corresponding to $\Delta F^{298} = -0.70$ kcal./mole. Although the entropy difference between *cis*- and *trans*-olefins in the hydrocarbon series is generally small,[25] it cannot be inferred that ΔS for the above process is similarly small. The data allow a limited analysis by the method of Allinger and Coke[26] whereby the associated enthalpy and entropy can be determined by a plot of ln K *vs.* $1/T$; in this manner, it was found that $\Delta H^{477} = -1.1 \pm 0.1$ kcal./mole and $\Delta S^{477} = -0.2 \pm 0.1$ e.u. It can be concluded that *cis*-**5** is stabilized over *trans*-**13** by electronic factors that overcome the large repulsive steric and dipole effects in the *cis* isomer. This appears to be the first example of a fumaronitrile–maleonitrile pair in which the maleonitrile is the isomer of lower energy. It is also interesting to note that the thermal and anion catalyzed (but see footnote 7) dimerization of methyl cyanodithioformate (**4**) gave largely *cis*-**5**. These results may, however, only reflect the kinetic outcome of these transformations.



13 5

Temp., °C.	Time, hr.	K
157	43	2.39
191	9	2.08
250	2.5	1.90

Unfortunately, it was not possible because of side reactions to determine accurate equilibrium constants in the salt series: *cis*-**3** ⇄ *trans*-**16** and *cis*-**8** ⇄ *trans*-**14**. It is clear from the data of Table I, however, that both **3** and **8** are stable relative to the corresponding *trans* isomers.

Bis-(tetramethylammonium)*trans*-**16** was isomerized very slowly to the *cis* isomer to the extent of 26% in 63 hours in aqueous solution at 110° under conditions where the corresponding *cis*-salt was unchanged. In less polar solvents, such as acetonitrile, bis-(tetramethylammonium) *cis*-**3**

---

[19] C. J. Timmons and S. C. Wallwork, *Chemistry & Industry*, 62 (1955).

[20] Phenylmaleonitrile, m.p. 86–87°, and phenylfumaronitrile, m.p. 42–43°, have recently been shown to have dipole moments of 7.98 and 2.71 D., respectively, by W. C. Schneider, *J. Am. Chem. Soc.*, **77**, 2796 (1955); also see W. F. Beech and H. A. Piggott, *J. Chem. Soc.*, 423 (1955).

[21] E. Knoevenagel and B. Bergdolt, *Ber.*, **36**, 2861 (1903).

[22] See N. R. Elred and D. M. Young, *J. Am. Chem. Soc.*, **75**, 4338 (1953); O. W. Cass, U. S. Patent 2,443,494.

[23] Unpublished observations of Dr. E. L. Martin of these laboratories.

[24] Other substituted fumaro- and maleonitrile pairs (not containing sulfur atoms) have been synthesized recently in this Laboratory and will be reported on in the future. In all cases, the thermodynamically stable isomer was the fumaronitrile.

[25] See tables in G. Janz, "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, Inc., New York, N. Y., 1958, pp. 169, 171.

[26] N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959).

isomerized to the *trans* isomer only to the extent of 25%, although most of the salt decomposed to tars in this solvent. The corresponding *trans* isomer decomposed completely under these conditions and no **3** or **16** could be recovered. It can be concluded that *cis*-**3** is chemically and configurationally stable relative to *trans*-**16** in both amphiprotic and aprotic solvents. Weakly coordinating cations (Na^+) are effective in accelerating the isomerizations **16** → **3** and **14**→**8**. It is probable that both **3** and **16** are strongly solvated in aqueous solution and charge dispersal may not be large. The central carbon–carbon bond must possess a high bond order, so that a large activation energy is encountered in geometrical isomerization.

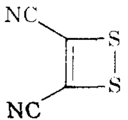
Some brief studies were also made of the influence of ultraviolet light on the configurational stability of the various isomers. It was found that *trans*-**13** is isomerized quantitatively in 12 hours in methanol solution to *cis*-**5** under broad spectrum ultraviolet irradiation. This may be compared with the essentially complete photoisomerization of diphenylfumaronitrile to diphenylmaleonitrile.[17] The value of the *cis/trans* ratio in the photochemical steady-state is somewhat dependent on the wave length of the light used and on the temperature[27]; however, it is usually observed that irradiation with ultraviolet light brings about isomerization of the more stable (thermodynamic) isomer to the less stable isomer or to a mixture in which the latter predominates.[27,28] This is borne out in the case of the diphenylfumaro- and -maleonitriles. This generalization does not hold for *cis*-**5** and *trans*-**13**.

It is tempting to relate the long wave length absorption of **5** and **13** with the transition causing isomerization. It was seen above that the ground state of *cis*-**5** lies approximately +0.05 e.v. below that of *trans*-**13**. This is in the correct direction for having the first excited states of **5** and **13** correspond to the state responsible for geometrical interconversion.[27] The long wave length absorptions of *cis*-**5** and *trans*-**13** involve energy changes of 3.64 and 3.41 e.v., respectively.

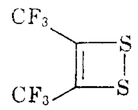
Although aqueous solutions of the pure sodium salts *cis*-**3** and *trans*-**16** were completely stable in the dark for several days, brief ultraviolet irradiation (broad spectrum) of oxygen-free, aqueous solutions of either isomer led to nearly identical solutions of their mixture. The ratio of isomers in the photochemical steady-state is *cis/trans* = 0.38 at 55° (beginning with **3**) and 0.36 (beginning with **16**), average value 0.37, and identical results (within experimental error) were obtained when the corresponding bis-(tetramethylammonium) salt of **16** was irradiated in aqueous solution. A curious anomaly was found in bis-(tetramethylammonium) dimercaptomaleonitrile, which under identical irradiation conditions underwent extensive decomposition. When the bis-(tetramethylammonium) and sodium salts of **3** and **16** were irradiated in ethanol solution, essentially the same results were obtained (see Experimental Section) as in water.

In summary, *cis*-**3**, as the disodium or bis-(tetramethylammonium) salt, emerges as a structure of configurational stability comparable to that of the *trans* isomer **16**, a structure which incorporates a much more favorable alignment of the strongly repulsive mercaptide poles and cyano dipoles. Unfortunately, none of the criteria applied above give an unequivocal answer as to which isomer is of lower energy. The spectral and polarographic studies revealed nothing that necessarily supports a cyclic formulation for the *cis* isomer, while the thermal and irradiation studies tend to support the view that some special stabilization exists.

One explanation of the unusual configurational stability of the dianion present in *cis*-**3** invokes consideration of structures involving sulfur–sulfur bonding as significant contributors to the ground state of **3**, as suggested above. In a later publication[8] evidence is presented for the intermediacy of the highly reactive dicyano-1,2-dithiete (**22**) in oxidations of **3** and **16**. Electronegatively substituted dithietes, *e.g.*, bis-(trifluoromethyl)-1,2-dithiete (**23**), have previously been synthesized in these laboratories.[29] The addition of two electrons to **22** can give rise to several electronic formulations, the lowest energy of which should represent salt **3**. This can be accomplished by: (a) ring-opening to give the resonance-stabilized dimercaptide **3**; (b) addition to the π-system resulting in a cyclic dianion with twelve π-electrons distributed over the four-membered ring and the cyano groups; (c) addition to a vacant d_π-molecular orbital extending over the two sulfur atoms, the repulsions of the formally localized negative charges on the sulfur atoms being offset by delocalization of the p_π-electrons into the cyano groups. d-Orbitals on the two sulfur atoms are oriented in the four-membered ring for maximum d_π overlap.



22



23

LCAO–MO calculations neglecting overlap were carried out for cases a, b and c employing coulomb and resonance parameters that in part were derived from studies in these laboratories on cyanocarbon anions and in part from the literature.[30,31] The results are not very sensitive to the parameter values, and the calculated resonance energies for cases a, b and c are 1.72 β_0, 3.30 β_0 and 1.96 $\beta_0 + \epsilon_{d\pi}$, respectively, where $\epsilon_{d\pi}$ is the energy of the new d_π sulfur–sulfur bond. The resonance energy of the uncharged dithiete **22** is 1.96 β_0. These calculations neglect repulsion energies in the charged and uncharged structures and can only be considered valid in the light of usual LCAO–MO theory. The formal neglect of interelectronic repulsion energy in small rings is an especially drastic

---

[27] G. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 3rd Edition, 1960, p. 356.

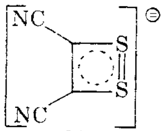
[28] G. Reid, *Chem. Revs.*, **12**, 205 (1958).

[29] C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960); C. G. Krespan, *ibid.*, **83**, 3434 (1961).

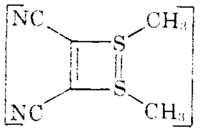
[30] M. J. Janssen, *Rec. trav. chim.*, **79**, 454, 464, 1006 (1960).

[31] In paper IV of this series a more detailed account of these calculations will be given. The parameter values chosen for the present study were: $\alpha_C = \alpha_0$, $\alpha_N = \alpha_0 + 1.5\beta_0$, $\alpha_S = \alpha_0 + 0.2\beta_0$, $\beta_{CC} = \beta_0$, $\beta_{CN} = 1.2\beta_0$, $\beta_{CS} = 0.6\beta_0$, $\beta_{SS} = 0.3\beta_0$.

approximation, and the resonance energy in case b must be much reduced since twelve p_π electrons are forced into an eight-atom system. There are further difficulties in selecting model structures on which to base resonance energy calculations. However, it can be seen that transfer of two electrons to dithiete 22 in a manner to preserve the ring (cases b and c) leads to energetically more favorable structures than the opened classical structure (case a). Estimates of the repulsions involved in case b indicate that the resonance energy may be negligible. We can thus conclude that if the interelectronic repulsion energy of case c is less than 0.24 $\beta_0 + \epsilon_{d\pi}$, the cyclic structure containing a d_π-bond, which can be written as 24, will be favored over the classical formulation in case a. The dotted lines refer to the usual 6 π-electron system and the d_π-bond is shown as a full line.



24



25

If d-orbital overlap between adjacent sulfur atoms is a factor to be considered in explaining the stability of the various dicyanodimercaptoethylene derivatives, it might be expected to play a role even in the covalent methyl derivative 5. The d- and p-orbitals are presumed to be partially mixed so that the overlapping hybrids are at least weakly populated. For instance, we might conceive pd^2-hybrids whose directional properties are correct to meet our requirements. This effect can become very significant if energy is to be gained since the 2p–3d separation is not prohibitively large in sulfur. Alternatively, the bonding could simply involve a non-hybridized representation such as 25 in which the ring contains four p-electrons. The solid lines here represent p_π-bonds.

The final decision on whether salt 3 exists as a resonance-stabilized dimercaptide of conventional structure 3 or as a dianion 24 possessing some degree of sulfur–sulfur bonding probably will be resolved only by X-ray studies.

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

Experimental[32]

Materials.—The DMF complex of sodium cyanodithioformate (1)[1] and disodium dimercaptomaleonitrile (3)[2] were prepared and purified as described in the literature. Salt 3 was recrystallized from absolute ethanol to constant ultraviolet extinction coefficient and was used in the form of a pale yellow, crystalline solid. The ultraviolet spectrum of salt 3 showed maxima in water at 272 (ϵ 7210) and 375 mμ (ϵ 16,200), in ethanol at 262 (ϵ 6290) and 376 mμ (ϵ 14,240), and in DME at 375 mμ (ϵ 2790). The extinction coefficient in DME was low and subject to a large error because of the very low solubility of 3 in this solvent. The procedure for the preparation of 1[1] could be modified to include acetamide, dimethylacetamide and N-methylpyrrolidone as solvents. The interaction of alkali metal cyanides with carbon disulfide was negligible in all solvents studied except those containing amide groups.

The DMF solvate of salt 1 showed nitrile absorption at 4.55 μ and the carbonyl band of the DMF-solvated complex was split into a sharp doublet at 6.00 and 6.06 μ. The normal carbonyl absorption of DMF occurs at 6.00 μ.

Infrared spectra were determined on a Perkin-Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ). Spectra were obtained in potassium bromide wafers and in Nujol mulls. The visible and ultraviolet spectra were determined by means of a Cary model 11 recording spectrophotometer. The polarographic oxidation measurements were carried out conventionally, and each salt was studied under several electrolyte and *p*H conditions in aqueous solution. The concentration range was 1 to 10 × $10^{-4}M$. Electrolytes included lithium perchlorate, sodium acetate and sodium sulfate, the latter in conjunction with Britton–Robinson buffers at *p*H 4–8. The results are recorded in the body of the paper.

Tetraethylammonium Cyanodithioformate (2). A. From Salt 1.—A solution of sodium cyanodithioformate DMF complex (1, 38.6 g., 0.100 mole) in boiling ethanol (100 ml.) was stirred while tetraethylammonium bromide (23.1 g., 0.110 mole) in boiling ethanol (50 ml.) was added over several minutes. The dark solid (23.5 g., 100%), which crystallized on cooling the mixture to 0°, was removed by filtration and recrystallized from ethanol. Salt 2 was obtained as lustrous brown crystals, m.p. 133–135°. No melting point is given in the literature.[1] The infrared spectrum showed, in addition to absorptions assigned to the tetraethylammonium ion, bands at 4.58 μ (CN) and 9.5–9.6 μ (C=S). The ultraviolet spectrum showed maxima at 380 (ϵ 11,100), 470 (ϵ 130) and 550 mμ (ϵ 16).

B. From Tetraethylammonium Cyanide[33] and Carbon Disulfide.—A solution of tetraethylammonium cyanide (4.8 g., 0.045 mole) in methylene chloride (85 ml.) was added with stirring over 1 hour to a solution of carbon disulfide (6.85 g., 0.090 mole, 100% excess) in methylene chloride (100 ml.). The brown color of the cyanodithioformate ion developed rapidly. The solution was then heated under reflux for 3 hours, cooled, and the solvent was removed under reduced pressure. The residue was a brown crystalline mass of 2, the crude yield of which was nearly quantitative. Recrystallization from hot ethanol gave pure 2, m.p. 133–135°.

Thermal Conversion of Salt 1 to Salt 3.—A sample of salt 1 (1.0 g., 0.0029 mole) was heated *in vacuo* at 130° for 2 hours. The initial brown melt turned to a yellow solid and sulfur sublimed onto cooler parts of the flask. The crystalline residue (0.5 g., *ca.* 100%) was characterized as pure disodium *cis*-3 by its infrared spectrum.

Methyl Cyanodithioformate (4).—A mixture of salt 2 (2.32 g., 0.010 mole) and methyl iodide (10 ml., excess) in acetonitrile (30 ml.) was stirred at room temperature for 1 minute followed by dilution with petroleum ether (50 ml.) and water (40 ml.). The three layers were separated and the aqueous layer containing tetraethylammonium iodide was discarded. The acetonitrile layer was extracted with several 20-ml. portions of petroleum ether and the extracts were combined. Petroleum ether was removed under a stream of dry nitrogen to leave 0.77 g. (65%) of a purple liquid. The ester is not very stable to fractionation; however, small samples were distilled through a short path still at 50–60° (1.0 mm.) to give a deep purple liquid, n^{25}D 1.625. The infrared spectrum of 4 showed absorptions at 3.43, 4.52, 7.11, 7.62, 8.76, 8.90, 9.85 and 10.17 μ. The ultraviolet spectrum showed maxima at 226 (ϵ 5100), 342 (ϵ 8750), and 530 mμ (ϵ 22).

Anal. Calcd. for $C_3H_3NS_2$: C, 30.74; H, 2.58; N, 11.95. Found: C, 31.61; H, 2.60; N, 11.53.

Conversion of Ester 4 to Bis-(methylmercapto)-maleonitrile. A. By Lithium Iodide.—A mixture of ester 4 (0.416 g., 0.00178 mole) and lithium iodide (5 mg.) in methylene chloride (2.0 ml.) was allowed to stand several days at room temperature. When the purple color was no longer visible, the sample was analyzed by quantitative infrared analysis. Only bis-(methylmercapto)-maleonitrile (5) was detected, along with absorptions assignable to 4. The conversion was 13% and none of the *trans* isomer 13 was

---

(32) All boiling points are uncorrected and melting points are corrected.

(33) The preparations of tetraethylammonium cyanide in the older literature are not reproducible, and the material used in this work was prepared by a reliable new synthesis which will be published by Dr. O. W. Webster of these laboratories.

detected. The physical and spectral constants of 5 and 13 are given below.

B. **By Tetraethylammonium Cyanide.**—A solution of tetraethylammonium cyanide[22] (1.56 g., 0.01 mole) in methylene chloride (50 ml.) was cooled in an ice-bath and stirred while a solution of ester **4** (1.17 g., 0.01 mole) in methylene chloride (10 ml.) was added dropwise over 30 minutes. The purple color of the methyl ester vanished immediately upon addition and the final color of the reaction mixture was yellow. The solution was stirred for 1 hour and evaporated *in vacuo* to afford a semi-solid mass. Crystallization of the residue from methyl ethyl ketone–ethyl acetate at −80° gave 1.31 g. (84% recovery) of tetraethylammonium cyanide. Chromatography of the filtrate on acid-washed alumina gave 0.27 g. (32%) of **5**. In another experiment employing 10 mole per cent of tetraethylammonium cyanide, the results were essentially unchanged. Infrared analysis in both cases showed only the presence of *cis*-**5**.

C. **Thermally.**—A sample of ester **4** (0.416 g., 0.00178 mole) was heated in a test-tube to *ca.* 120° at which point the liquid began to boil and the temperature rose spontaneously to 165° during which time the purple color faded. The tube was allowed to cool and the contents crystallized. Quantitative infrared analysis indicated a 47–53% conversion to *cis*-**5** and 1–5% to *trans*-**13**.

D. **By Irradiation.**—A solution of ester **4** (1.17 g., 0.01 mole) in methylene chloride (10 ml.) in a quartz tube was irradiated with a mercury vapor lamp for 3 days. The purple color had disappeared at the end of this period. The sample was evaporated to dryness under reduced pressure and the residue was chromatographed on acid-washed alumina. There was obtained 0.20 g. (23.5%) of *cis*-**5**, and 0.23 g. (19.5%) of ester **4** was recovered.

Bis-(tetramethylammonium)-dimercaptomaleonitrile.—A solution of disodium *cis*-**3** (0.50 g., 0.0027 mole) in methanol (2 ml.) was added to a solution of tetramethylammonium chloride (0.62 g., 0.0057 mole) in methanol (1 ml.). Sodium chloride was removed by filtration and the filtrate was evaporated to half-volume under reduced pressure. Isopropyl alcohol was added dropwise and a yellow micro-crystalline solid separated, 0.60 g. (78%). The salt was very hygroscopic and was difficult to purify further. Further purification was effected by dissolving the product in absolute ethanol (2 ml.) at room temperature, adding a few drops of isopropyl alcohol, and chilling the solution in Dry Ice. The fine yellow solid was collected and dried under reduced pressure at 100° for 2 hours. The infrared spectrum showed strong bands at 4.62, 6.78, 7.17, 9.07, 10.52 and 11.67 μ. Satisfactory analyses could not be obtained and contamination by sodium chloride and tetramethylammonium chloride was evident from elemental analysis.

Anal. Calcd. for $C_{12}H_{24}N_4S_2$: C, 49.97; H, 8.39. Found: C, 46.72; H, 8.13; Na, 0.92.

Methylation of Disodium *cis*-**3.**—A mixture of salt **3** (1.86 g., 0.010 mole) and methyl iodide (3.12 g., 0.022 mole) in methanol (20 ml.) was stirred for 2 hours, and water (20 ml.) was added. Crude *cis*-**5** (1.63 g., 97%) was separated and recrystallized from ethanol as pale yellow needles, m.p. 99°. Similar methylations were carried out in water, ethanol and DME, and high yields of pure *cis*-**5** were obtained. When the methylation was carried out by dropwise addition of methyl iodide over several hours to an alcoholic solution of salt **3**, the same result was obtained. Similarly, methylation of the bis-(tetramethylammonium) salt of *cis*-**3** in various solvents gave high yields of only *cis*-**5**.

The infrared spectrum of **5** showed characteristic bands at 6.60 (C═C, str.) and 8.52 μ. The spectrum of the crude product obtained in all of the methylation reactions showed the absence of any of *trans* isomer **13** which absorbs strongly at 12.33 μ (see below).

Bis-(benzoylmercapto)-maleonitrile (**6**).—Benzoyl chloride (4.51 g., 0.032 mole) in DME (5 ml.) was added over 40 minutes to a suspension of salt **3** (3.0 g., 0.016 mole) in DME (30 ml.) at 0°. The mixture was stirred for an additional 1.5 hours and was filtered. The filtrate was diluted with an equal volume of petroleum ether and chilled in Dry Ice. The dibenzoyl derivative (4.0 g., 71%) separated as tan needles, m.p. 118–122°. Recrystallization from benzene raised the melting point of pure **bis-(benzoylmercapto)-maleonitrile** (**6**) to 118–123°.

Anal. Calcd. for $C_{18}H_{10}N_2O_2S_2$: C, 61.69; H, 2.88; N, 8.00. Found: C, 61.76; H, 3.09; N, 8.01.

1-Methylmercapto-2-benzoylmercaptomaleonitrile (**7**).—A solution of methyl iodide (7.65 g., 0.054 mole) in DME (20 ml.) was added over 30 minutes to a stirred suspension of salt **3** (10 g., 0.054 mole) in DME (50 ml.) at 0°. When the addition was complete, a solution of benzoyl chloride (7.60 g., 0.054 mole) in DME (15 ml.) was added over 15 minutes. The mixture was filtered and the filtrate evaporated to dryness *in vacuo*. The crude product was recrystallized from benzene–cyclohexane and then from carbon tetrachloride to give 8.80 g. (63%) of **1-methylmercapto-2-benzoylmercaptomaleonitrile** (**7**) as tan crystals, m.p. 107–108.5°.

Anal. Calcd. for $C_{12}H_8N_2OS_2$: C, 55.43; H, 3.10; N, 10.78. Found: C, 55.76; H, 3.30; N, 10.97.

1-Sodiomercapto-2-methylmercaptomaleonitrile (**8**).—A suspension of **7** (1.00 g., 0.0039 mole) in methanol (10 ml.) was stirred and cooled to −20°. Addition of sodium methoxide (0.21 g., 0.0039 mole) gave a homogeneous orange solution. The solvent and methyl benzoate were lyophilized leaving a yellow solid, which was washed repeatedly with cyclohexane and ether. The crude salt **8** was purified by precipitation from acetonitrile solution with methylene chloride. After the solid was dried at 80° *in vacuo*, a nearly quantitative yield of **1-sodiomercapto-2-methylmercaptomaleonitrile** (**8**) was obtained. Characteristic bands occurred at 6.80, 8.61 and 11.65 μ.

Anal. Calcd. for $C_5H_3N_2S_2Na$: C, 33.70; H, 1.69; S, 36.00. Found: C, 33.72; H, 2.01; S, 36.27.

Methylation of Salt 8.—To a solution of salt **8** (0.200 g., 0.0011 mole) in methanol (4 ml.) was added over 3 minutes a solution of methyl iodide (0.340 g., 0.0024 mole) in methanol (5 ml.). The solution was evaporated to dryness under reduced pressure and the residue was extracted with methylene chloride. The solvent was removed and there was obtained 0.173 g. (91%) of *cis*-**5**. Quantitative infrared analysis of a 15% methylene chloride solution showed it to contain 93% *cis*-**5**. The *trans* isomer **13** could not be detected. This technique has been shown capable of detecting *ca.* 2% of *trans*-**13**. A similar methylation in acetonitrile gave pure *cis*-**5** in 87% yield. When the rate of addition of methyl iodide was decreased and when the methylation was carried out in other solvents, only *cis*-**5** was isolated or detected.

Disodium *trans-trans*-**Bis(2-mercapto-1,2-dicyanovinyl) Disulfide** (**10**).—A suspension of salt **3** (10.0 g., 0.0538 mole) in dry DME (80 ml.) was stirred and cooled to 0°. Over 15 minutes, bromine (4.40 g., 0.0275 mole) was added, and after 1 hour the mixture was evaporated *in vacuo* to a sirup. Water (2 ml.) followed by methylene chloride (140 ml.) was added dropwise with stirring. Subsequently, ether (600 ml.) was added slowly and the precipitated orange solid was removed by filtration and dried. The crude product was recrystallized from tetrahydrofuran (65 ml.) to give a first crop of 4.40 g. (50%) of *trans-trans*-**10**. The filtrate was reduced to one-half volume and was chilled at 0° for 2 days. In this manner a second crop of 1.90 g. (22%) of **10** was obtained. The infrared spectra of the two crops (total yield 72%) were identical.

In a similar manner thionyl chloride was employed as oxidizing agent. A suspension of salt **3** (35.0 g., 0.188 mole) in DME (200 ml.) was stirred and cooled to 0°. Over 30 minutes thionyl chloride (11.2 g., 0.094 mole) in DME (35 ml.) was added. The red suspension was filtered and the filtrate was evaporated to a sirup, which was stirred with methylene chloride (1 l.). The red-brown solid was filtered, washed with methylene chloride and dried. The crude product was recrystallized twice from acetonitrile at −20°. There was obtained only 1.7 g. of *trans-trans*-**10** by this procedure. The salt was dried at 56° *in vacuo*, but satisfactory analyses could not be obtained.

Anal. Calcd. for $C_8N_4S_4Na_2$: C, 29.47; N, 17.19; S, 39.34; Na, 14.10. Found: C, 28.42; N, 16.99; S, 42.09; Na, 12.50.

The main absorption bands occurred at 4.47, 4.52, 6.98, 8.75, 9.78 and 11.87 μ. The ultraviolet spectrum of *trans-trans*-**10** showed maxima in water at 365 (ε 19,400) and 408 mμ (ε 9450), in ethanol at 379 (ε 18,450) and 408 mμ (ε 14,870), and in DME in 389 (ε 12,320) and 420 mμ (ε 11,210).

Other studies showed that when the addition of thionyl chloride was complete, the ultraviolet spectrum was characteristic of *cis-cis*-**9**, which rapidly isomerized to *trans-trans*-**10**.

The disodium salt was converted to the bis-(tetramethylammonium) salt by treating a concentrated solution of disodium *trans-trans*-**10** with tetramethylammonium chloride in methanol. The product was recrystallized from methanol to give bright orange leaflets, m.p. 196–197° dec. The infrared spectrum showed strong bands at 4.49, 4.53 (doublet), 6.70, 7.04, 8.80, 9.80, 10.48 and 11.78 μ.

Anal. Calcd. for $C_{16}H_{24}N_6S_4$: C, 44.83; H, 5.64. Found: C, 44.93; H, 5.63.

Oxidation of Salt 3 with Iodine.—A solution of disodium *cis*-**3** (5 g., 0.027 mole) in ethanol (25 ml.) and methanol (25 ml.) was stirred at 0° while a solution of iodine (3.41 g., 0.014 mole) in ethanol (40 ml.) was added over 30 minutes. The mixture was evaporated to dryness under reduced pressure to give a red-orange solid. Attempts to remove the coprecipitated sodium iodide from the product were only partially successful. The crude yield was about 50% and the infrared spectrum was virtually identical to that of the product obtained in the thionyl chloride oxidation.

2,3-Dicyano-5,6-dihydro-1,4-dithiin.—A suspension of salt **3** (3.0 g., 0.016 mole) and ethylene dibromide (3.0 g., 0.016 mole) in DME (30 ml.) was stirred for 2 hours at room temperature and was then poured into water (200 ml.). The precipitate was collected by suction filtration and was washed with water and dried. The yield of cream colored solid melting at 130–132° was 2.22 g. (82%). After recrystallization from methylene chloride–methylcyclohexane, pure **2,3-dicyano-5,6-dihydro-1,4-dithiin** melted at 133–135°. The infrared spectrum showed a strong nitrile doublet at 4.46–4.49 μ and (C═C) stretching at 6.65 μ. Other characteristic bands occurred at 7.03, 8.57, 8.85 and 11.90 μ. The ultraviolet spectrum in 50% aqueous acetic acid showed maxima at 262 (ε 5800), 340 (ε 9000) and 353 mμ (ε 10,800).

Anal. Calcd. for $C_6H_4N_2S_2$: C, 42.89; H, 2.40; S, 38.17. Found: C, 42.98; H, 2.45; S, 38.08.

Disodium *cis-cis*-Bis-(2-mercapto-1,2-dicyanovinyl) Disulfide (9).—To a stirred suspension of salt **3** (1.00 g., 0.0054 mole) in DME (10 ml.) was added in one portion 1,1,2,2-tetrabromoethane (0.94 g., 0.0029 mole) in DME (4 ml.). The mixture was stirred for 3 minutes and then filtered rapidly. The filtrate was quickly evaporated to dryness *in vacuo*. Methylene chloride (60 ml.) was added to the residue and the mixture deposited a yellow-orange solid which was filtered and washed with methylene chloride. The yield of **9** was 0.27 g. (31%). The insoluble solid from the reaction mixture was suspended in fresh DME (10 ml.) and treated again for 3 minutes with 1,1,2,2-tetrabromoethane (0.94 g.). Repetition of the procedure afforded an additional 0.28 g. (32%) of salt **9**. A sample (0.20 g.) of the crude salt was dissolved in DME (1.5 ml.), the solution was filtered, and the salt was precipitated by the addition of methylene chloride (20 ml.) and dried at 80° *in vacuo*. An essentially quantitative recovery of **disodium *cis-cis*-bis-(2-mercapto-1,2-dicyanovinyl) disulfide (9)** was obtained. The salt could not be recrystallized because of isomerization to **10**. The infrared spectrum of *cis-cis*-**9** had characteristic bands at 4.58 (C≡N), 6.87 (C═C) and 8.68 μ. Medium absorptions appeared at 9.03, 9.41, 9.56 and 11.84 μ. Medium absorptions appeared at 9.03, 9.41, 9.56 and 11.84 μ. *trans-trans*-**10** had strong absorptions at 4.47–4.52, 6.97 and 8.75 μ, and medium bands at 9.78 and 11.87 μ. Analysis was obtained on the crude material.

Anal. Calcd. for $C_8N_4S_4Na_2$: C, 29.44; H, 0.00; N, 17.18; S, 39.30. Found: C, 29.04; H, 2.23; N, 15.54; S, 37.51.

In a similar experiment, 1,1,2,2-tetrabromoethane (55.0 g., 0.159 mole) was added over 30 minutes to a suspension of salt **3** (30.0 g., 0.161 mole) in DME (200 ml.). After 1.5 hours the reaction mixture was filtered, and the filtrate was distilled to dryness *in vacuo*. The distillate was dried and redistilled to obtain 7.28 g. (49%) of 1,2-dibromoethylene. Infrared spectral analysis showed the product was approximately a 1:1 mixture of *cis*- and *trans*-1,2-dibromoethylene. Bands at 6.35, 8.02 and 13.40 μ characterized the *cis* isomer, and the strong bands at 11.1–11.2 μ, the *trans* isomer.

The oxidation of salt **3** with tetrabromoethane was very slow in tetrahydrofuran and in methanol and only low conversions of salt **9** were isolated. Both *cis-cis*-**9** and *trans-trans*-**10** could be isolated unchanged from DME solutions containing the tetrabromoethane.

The bis-(tetramethylammonium) salt of *cis-cis*-**9** was prepared from the disodium salt with tetramethylammonium chloride in methanol solution. The yellow crystalline solid melted at 190–195° dec. The infrared spectrum showed absorptions at 4.51, 4.57, 6.72, 6.83, 8.72, 9.00, 9.57, 10.52 and 11.81 μ.

Isomerization of *cis-cis*-9 to *trans-trans*-10.—A solution of *cis-cis*-**9** (0.2 g.) in DME (5 ml.) was allowed to stand at 25° for 2 hours. The solvent was removed under reduced pressure at room temperature to give a red sirup which solidified when triturated with methylene chloride. There was obtained 0.18 g. of an orange solid whose infrared spectrum showed it to be nearly pure *trans-trans*-**10**. A few of the stronger absorption bands of *cis-cis*-**9** were still evident, and it was estimated that conversion to **10** was approximately 95% complete.

Methylation of *trans-trans*-10. A. Methyl Sulfate.—Recrystallized *trans-trans*-**10** (0.50 g., 0.00153 mole) in 5 ml. of water was stirred at room temperature while dimethyl sulfate (0.38 g., 0.00301 mole) was added. A yellow precipitate formed rapidly and after 5 minutes the solid was collected by filtration and washed with water. The crude product (0.29 g., 61%) melting at 107–123° was recrystallized from methylene chloride–methylcyclohexane to give a high recovery of pure ***trans-trans*-bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide (12)** as golden yellow leaflets, m.p. 123–126°. The infrared spectrum of **12** showed a double bond stretching absorption at 6.67 μ, and a strong band at 8.72 μ was useful in characterizing this isomer in mixtures.

Anal. Calcd. for $C_{10}H_6N_4S_4$: C, 38.69; H, 1.95; N, 18.05. Found: C, 38.89; H, 2.20; N, 17.99.

B. Methyl Iodide.—A mixture of methyl iodide (0.38 g., 0.0027 mole) and recrystallized *trans-trans*-**10** (0.19 g., 0.00058 mole) in DME (4 ml.) was stirred for 30 minutes at room temperature. The mixture was diluted with methylene chloride and the resulting solution was washed with dilute aqueous sodium bisulfite solution to destroy the liberated iodine. The infrared spectrum of the yellow solid (0.17 g., 86%), m.p. 120°, remaining after evaporation of the solvent, indicated a mixture of *cis*-**5** (<7%) and *trans*-**13** (> 93%). The characterization of *trans*-**13**, m.p. 118–119° is given below under **Methylation of Disodium *trans*-16.**

Methylation of *cis-cis*-9. A. Methyl Sulfate.—Over a 30-second period solid *cis-cis*-**9** (0.10 g., 0.00031 mole) was added to a stirred solution of dimethyl sulfate (0.058 ml., 0.00061 mole) in tetrahydrofuran (3 ml.). After 20 minutes the reaction mixture was filtered and the filtrate was evaporated to dryness. Evaporation of a methylene chloride extract gave a semi-solid yellow product whose infrared spectrum showed it to be a mixture of *cis-cis*-**11** and *trans-trans*-**12** in a ratio of about 2:1. The sample of *cis-cis*-**9** used in the experiment was free from *trans-trans*-**10**, and the mixture of isomers resulted from the rapid isomerization of **9** to **10** before methylation. The synthesis and characterization of pure *cis-cis*-**11** are reported below.

B. Methyl Iodide.—A mixture of methyl iodide (0.057 g., 0.00040 mole) and disodium *cis-cis*-**9** (0.030 g., 0.000092 mole) in dry DME (0.5 ml.) liberated iodine at once, and after 30 minutes methylene chloride (20 ml.) was added. The solution was washed with dilute aqueous sodium bisulfite solution and water and was dried. Evaporation of the solvent gave 0.025 g. (76%) of a yellow crystalline mass whose infrared spectrum showed it to consist of 90% *cis*-**5** and 10% *trans*-**13**.

***cis-trans*-Bis-(2-methylmercapto-1,2-dicyanovinyl) Disulfide.**—A freshly prepared solution of dicyano-1,2,3-trithiole-2-oxide[13] (0.10 g., 0.00053 mole) in tetrahydrofuran (2 ml.) was added over 10 seconds to a suspension of disodium *trans*-**16** (0.10 g., 0.00053 mole) in tetrahydrofuran (2 ml.). After 1 minute dimethyl sulfate (0.14 g., 0.00111 mole) was added to the deep red solution. The mixture was filtered after 15 minutes and the filtrate was evaporated *in vacuo*. Cold storage and scratching did not induce crystallization. A solution of the product was passed rapidly through a short column of acid-washed alumina using ether as eluent to give a clear amber oil.

Anal. Calcd. for $C_{10}H_6N_4S_4$: C, 38.69; H, 1.95. Found: C, 38.91; H, 2.13.

The infrared spectrum was virtually superimposable on that of a 1:1 mixture of *cis-cis*-**11** and *trans-trans*-**12**. The ultraviolet spectrum of the *cis-trans* isomer showed a single maximum at 345 mμ (ε 17,680) in ethanol.

An ether solution of the *cis-trans* isomer deposited no solid when it was chilled in a Dry Ice–acetone-bath and seeded with both *cis-cis*-**11** and *trans-trans*-**12**. In another experiment a 1:1 mixture of *cis-cis*-**11** and *trans-trans*-**12** could be separated to the extent of at least 85% by simple fractional crystallization from ether.

Potassium Iodide-catalyzed Interconversion of *cis-cis*-11 and *trans-trans*-12.—A solution of *cis-cis*-11 (0.03 g., 0.00010 mole) in DME (2 ml.) containing powdered potassium iodide (0.001 g., 0.00006 mole) was stirred at 25° for 45 minutes. The solvent was removed at 25°, and the residue was triturated with ether. The infrared spectrum of the totally recovered product indicated a mixture of *cis-cis*-11 and *trans-trans*-12, in a ratio of *ca.* 2:1 and was superimposable on that of a synthetic 2:1 mixture of 11 and 12. Repetition of this experiment employing the higher melting isomer *trans-trans*-12 gave a product whose infrared spectrum was indistinguishable from that obtained by starting with the lower melting isomer *cis-cis*-11. In both cases the mixture of 11 and 12 could be separated to the extent of *ca.* 85% by fractional crystallization or, better, by seeding with either pure isomer.

Thermal Isomerization of *cis-cis*-11, *trans-trans*-12 and the *cis-trans* Isomer.—Small samples of pure *cis-cis*-11 and *trans-trans*-12 were heated at reflux in carbon tetrachloride solution for periods of about 2 hours. In each case the equilibrium mixture of 11 and 12 was obtained, the ratio of 11:12 being 2:1, as determined by infrared spectral analysis and by low temperature fractional crystallization from ether.

When a sample of the corresponding *cis-trans* isomer was heated under the same conditions, no change was noted in the spectrum, which was superimposable on that of a 1:1 mixture of 11 and 12. The recovered material was presumably pure *cis-trans* isomer as discussed in the text.

The ultraviolet spectrum of the product of thermal isomerization was very similar to that of a synthetic mixture of 11 and 12 and appeared different from that of the corresponding *cis-trans* isomer. The differences were very difficult to translate into quantitative terms by this technique.

Similar results were observed when the three isomers were held in the melt for 2 hours.

Oxidation of Salt 8. A. Potassium Ferricyanide.—A solution of potassium ferricyanide (0.34 g., 0.0010 mole) in water (5 ml.) was added to a solution of sodium salt 8 (0.18 g., 0.0010 mole) in water (2 ml.) at 0°. A yellow solid began to separate immediately. After 10 minutes the reaction mixture was filtered, and the product was washed with water. The yield of yellow solid melting at 96–99° was 0.18 g. (76%). A solution of the crude product in methylene chloride was treated with Darco, filtered, diluted with an equal volume of ether and chilled to −80°. An excellent recovery of pure *cis-cis*-**bis-(2-methylmercapto-1,2-dicyanovinyl) disulfide** (11) was obtained. The melting point of the yellow crystals was very dependent on the rate of heating. When placed on a block at 99°, the solid melted at 102–104°.

Anal. Calcd. for $C_{10}H_6N_4S_4$: C, 38.69; H, 1.95; N, 18.05. Found: C, 39.04; H, 2.20; N, 18.04.

The principal bands of the infrared spectrum of 11 are at 4.52, 6.68 (C=C) stretching, 7.02, 7.56, 8.56 and 11.82 μ. The spectrum of *cis-cis*-11 is expectedly very close to that of *trans-trans*-12. The two isomers are most clearly distinguishable by the bands at 8.56 and 11.82 μ (11) and those at 8.72 and 12.28 (12).

B. **Thionyl Chloride.**—A suspension of sodium salt 8 (0.30 g., 0.0017 mole) in DME (10 ml.) was stirred and cooled in an ice-bath, and thionyl chloride (0.12 g., 0.0010 mole) in DME (2 ml.) was added over 3 minutes. The mixture was stirred for 30 minutes and then evaporated to dryness under reduced pressure. The residue was extracted with methylene chloride to give an oil whose infrared spectrum indicated a mixture of *cis-cis*-11 and *trans-trans*-12 in a ratio of 55:45.

C. **Tetracyanoethylene.**—Tetracyanoethylene (0.21 g., 0.0016 mole) in tetrahydrofuran (3 ml.) was added over 5 minutes to a stirred suspension of sodium salt 8 (0.30 g., 0.0017 mole) in tetrahydrofuran (3 ml.). After 5 minutes a maroon solid (shown to be sodium tetracyanoethylene anion-radical) was removed by filtration, and the filtrate was evaporated *in vacuo*. From a methylene chloride extract there was obtained 0.21 g. (81%) of a viscous orange sirup, whose infrared spectrum showed a ratio of *cis-cis*-11 to *trans-trans*-12 of 2:1.

D. **Bromine.**—A solution of salt 8 (0.18 g., 0.0010 mole) in DME (3 ml.) was stirred at 0° and a solution of bromine (0.08 g., 0.00050 mole) in DME (1 ml.) was added rapidly. After 10 minutes the mixture was filtered and the filtrate was evaporated under reduced pressure. Recrystallization of the brown oil from methylene chloride–methylcyclohexane gave 0.109 g. (70%) of 11, m.p. 95–98°. A mixed melting point with the product obtained in the potassium ferricyanide oxidation showed no depression.

Oxidation of Salt 14. A. Sodium Salt.—A solution of potassium ferricyanide (0.09 g., 0.00027 mole) in water (1 ml.) was added to a freshly prepared solution of salt 14 (0.05 g., 0.00024 mole) in 3 ml. of water. The preparation of salt 14 is given below. A yellow cloudiness developed instantly and after a few minutes, the solid which coagulated was collected by filtration and washed with water and dried. The yield of the mixture of 11 and 12 was 0.04 g. (92%). The infrared spectrum showed the solid to be a mixture of *cis-cis*-11 and *trans-trans*-12 in the ratio of 1:3. The sample of salt 14, which is very difficult to obtain stereochemically pure, probably contained sufficient *cis*-8 to account for the appearance of 25% of *cis-cis*-11 in the product.

B. **Tetramethylammonium Salt.**—A solution of the tetramethylammonium salt 14 (0.030 g., 0.00013 mole) in water (1 ml.) was added over 30 seconds to a cold, stirred solution of potassium ferricyanide (0.050 g., 0.00015 mole) in water (2 ml.). A yellow precipitate which formed immediately was collected, washed, and dried (0.020 g. (99%)). Analysis by infrared showed the product to be essentially pure *trans-trans*-12. The maximum contamination by *cis-cis*-11 was <5%.

Bis-(benzoylmercapto)-fumaronitrile (15).—A solution of *trans-trans*-10 (6.0 g., 0.018 mole) in dry tetrahydrofuran (40 ml.) was stirred and cooled at 0° while a suspension of potassium borohydride (1.95 g., 0.037 mole) in cold methanol (60 ml.) was added over 30 seconds. After 10 minutes, a solution of benzoyl chloride (12.9 g., 0.092 mole) in tetrahydrofuran (30 ml.) was added in one portion. The mixture was stirred for 15 minutes at 25° and was then evaporated to dryness *in vacuo*. The solid residue from an extraction with methylene chloride (100 ml.) was diluted with 150 ml. of ether and 50 ml. of methylcyclohexane. The solution was chilled for 1 hour at −80° and deposited 8.95 g. (70%) of tan crystals, m.p. 141–148°. Two similar recrystallizations gave **bis-(benzoylmercapto)-fumaronitrile** (15), m.p. 127–157°. When placed on a block at 140° (2°/min.) a sample melted at 144–150°. The wide melting point range is probably due to isomerization on the melting point block. The infrared spectrum of *trans*-15 is similar to that of *cis*-6 but there are bands at 9.28, 9.55 and 12.38 μ which are absent in 6. In addition, there are slight frequency shifts of common bands. On the basis of the infrared spectrum, the product appeared to contain none of the *cis* isomer.

Anal. Calcd. for $C_{18}H_{10}N_2O_2S_2$: C, 61.69; H, 2.88; N, 8.00. Found: C, 61.76; H, 3.22; N, 8.17.

Disodium Dimercaptofumaronitrile (16).—A suspension of bis-(benzoylmercapto)-fumaronitrile (15) (2.50 g., 0.0071 mole) in methanol (50 ml.) was stirred and cooled to −25 to −20°. A solution containing sodium (0.33 g., 0.0143 mole) in methanol (5 ml.) was added, and after 45 minutes most of the solid had dissolved. The reaction mixture was evaporated to dryness *in vacuo* at −20 to −15°. The residue was washed thoroughly with ether and with methylene chloride to remove methyl benzoate. The resulting solid was dissolved in the minimum amount of methanol, decolorized, filtered and precipitated by the slow addition of ether. After two similar purifications there was obtained 0.77 g. (50%) of **disodium dimercaptofumaronitrile** (16).

Anal. Calcd. for $C_4N_2S_2Na_2$: C, 25.80; N, 15.05. Found: C, 25.72; N, 15.03.

The infrared spectrum of *trans*-16 is extremely simple having strong bands at 4.51 (C≡N), 9.88 and 12.11 μ and several very weak bands, possibly due to impurities, in the 6–7 μ region.

Bis-(tetramethylammonium)-Dimercaptofumaronitrile.—A solution of disodium *trans*-16 (1.88 g., 0.0101 mole) in methanol (15 ml.) was added to a solution of tetramethylammonium chloride (2.32 g., 0.0212 mole) in methanod (8 ml.) at 25°. The solution was chilled in an ice-bath and 0.73 g. of sodium chloride was removed by filtration. The filtrate was diluted with isopropyl alcohol (25 ml.), and 2.0 g. (69%) of tan crystals which separated were removed by filtration. The product was dissolved in the smallest quantity of methanol and caused to crystallize by the addition of isopropyl alcohol. There was obtained 1.48 g. (51%), of **bis-(tetramethylammonium)-dimercaptofumaronitrile** m.p. 154–156° dec. Satisfactory analyses could not be obtained and contamination by tetramethylammonium chloride was evident from elemental analysis. The infrared spectrum had strong bands at 4.60, 6.77, 10.14, 10.50 and 12.35 μ.

Anal. Calcd. for $C_{12}H_{24}N_4S_2$: C, 49.97; H, 8.39. Found: C, 48.84; H, 8.27.

Methylation of Disodium *trans*-16 with Methyl Iodide. **A.**—Methyl iodide (1.14 g., 0.0080 mole) was added in one portion to a solution of disodium *trans*-**16** (0.10 g., 0.00054 mole) in methanol (3 ml.), and after 15 minutes the solvent was removed *in vacuo*. The residue obtained from extraction with methylene chloride was evaporated to give 0.08 g. (88%) of a yellow solid, whose infrared spectrum showed its composition to be 85:15 of *trans*-**13**:*cis*-**5**. *trans*-**13** was obtained free of the *cis* isomer by fractional recrystallization from ethanol. Pure **bis-(methylmercapto)-fumaronitrile** (**13**) was obtained as yellow crystals, m.p. 118–119°.

Anal. Calcd. for $C_6H_6N_2S_2$: C, 42.32; H, 3.55; N, 16.46; S, 37.67. Found: C, 42.43; H, 3.79; N, 16.66; S, 37.93.

B.—A solution of methyl iodide (0.080 g., 0.00056 mole) in methanol (4 ml.) was added dropwise at 25° over 30 minutes to a stirred solution of disodium *trans*-**16** (0.00027 mole) in methanol (4 ml.). After 10 minutes the reaction mixture was worked up as in A. Infrared analysis of the crude product showed *trans*-**13**:*cis*-**5** (30:70).

C.—A freshly prepared solution of disodium *trans*-**16** (0.020 g., 0.00011 mole) in water (1 ml.) was added over 30 seconds to a stirred mixture of methyl iodide (1.15 g., 0.0081 mole), acetone (3 ml.) and water (3 ml.). After 10 minutes the product was worked up as described in A. The infrared spectrum of the crude product showed *trans*-**13**:*cis*-**5** to be > 95:<5.

D.—Procedure A was repeated except that disodium *trans*-**16** was added *to* methanolic methyl iodide. The ratio of *trans*-**13**:*cis*-**5** was approximately 95:5. Thus when *trans*-**16** is in solution for the shortest possible time before methylation, high yields of almost pure *trans*-dimethyl derivative can be obtained.

1-Benzoylmercapto-2-methylmercaptofumaronitrile (17).—A solution of disodium *trans*-*trans*-**12** (1.02 g., 0.0033 mole) and benzoyl chloride (1.31 g., 0.0094 mole) in tetrahydrofuran (50 ml.) was stirred and cooled to −20°. A solution of potassium borohydride (0.40 g., 0.0074 mole) in methanol (90 ml.) was precooled to −20° and added over 5 seconds. The mixture was allowed to warm to 25° and stand 15 minutes. The volatile components were removed under reduced pressure and the residue was extracted thoroughly with methylene chloride. The residue (1.05 g., 61%) recovered from the extract was recrystallized from ether at −80°. Pure **1-benzoylmercapto-2-methylmercaptofumaronitrile** (**17**), m.p. 74.5–75.5°, was obtained as hard yellow needles after two recrystallizations. The infrared spectrum of *trans*-**17** was very similar to that of *cis*-**7**. Characteristic new absorptions in **17** occurred at 8.72, 10.18, 10.30 and 12.21 μ.

Anal. Calcd. for $C_{12}H_8N_2OS_2$: C, 55.36; H, 3.10; N, 10.76. Found: C, 55.51; H, 3.34; N, 10.42.

1-Sodiomercapto-2-methylmercaptofumaronitrile (14).—To a stirred suspension of 1-benzoylmercapto-2-methylmercaptofumaronitrile (**17**) (0.30 g., 0.0012 mole) in methanol (5 ml.) at 0° was added 0.40 ml. of a solution of sodium methoxide prepared from sodium (3.29 g., 0.143 mole) in dry methanol (50 ml.). The solid dissolved within a few seconds and the solvent was removed *in vacuo* at 0°. The resulting sirup was stirred with ether–methylene chloride to remove methyl benzoate. The yellow solid which remained was washed well with ether and dried. No suitable solvent was found for recrystallization of **14** and satisfactory analyses of the sodium salt could not be obtained. The infrared spectrum of **14** was very similar to that of the *cis* isomer **8**, but the two were distinguishable in the 12 μ region. *trans*-**14** has a strong band at 12.12 μ, (absent in **8**), and *cis*-**8** absorbs similarly at 11.65 μ (present weakly in **14**). Other absorptions occur at 4.53, 4.58, 7.06, 8.58, 8.76, 9.84 and 10.26 μ. *trans*-**14** was obtained pure as the tetramethylammonium salt.

Tetramethylammonium 1-Mercapto-2-methylmercaptofumaronitrile.—A solution of methyl iodide (0.42 ml., 0.0068 mole) in methanol (45 ml.) was added over 20 minutes to a solution of bis-(tetramethylammonium)-dimercaptofumaronitrile (1.82 g., 0.00658 mole) in methanol (16 ml.). The mixture was allowed to stand for 1 hour at 25°, was filtered, and the filtrate was evaporated to a semi-solid mass. The residue was extracted thoroughly with methylene chloride, and the extracts were evaporated. The residue was dissolved in the minimum amount of methanol, and ether was added dropwise. The sirup which separated crystallized rapidly. This purification was repeated to give 0.55 g. (38%) of orange, crystalline **tetramethylammonium 1-mercapto-2-methylmercaptofumaronitrile**, m.p. 78–80°.

Anal. Calcd. for $C_9H_{15}N_3S_2$: C, 47.13; H, 6.59; N, 18.32. Found: C, 47.49; H, 7.00; N, 18.63. The infrared spectrum showed strong absorptions at 4.52, 4.60, 6.78, 7.00, 7.68, 8.84, 9.92, 10.40, 10.57 and 11.98 μ.

Methylation of Salts of 1-Mercapto-2-methylmercaptofumaronitrile. A. Sodium Salt.—When sodium *trans*-**14** was treated with an excess of methyl iodide in methanol at 25°, a good yield of a mixture of *cis*-**5** and *trans*-**13** was obtained. Infrared analysis indicated the *trans*/*cis* ratio was approximately 0.4.

B. Tetramethylammonium Salt.—The tetramethylammonium salt corresponding to *trans*-**14** (0.040 g., 0.00017 mole) was dissolved in methanol (2 ml.) and the solution was allowed to stand at 25° for 6 hours. One-half of the solution was subsequently methylated with excess methyl iodide and work-up in the usual manner gave a high yield of a mixture of *trans*-**13** (95%) and *cis*-**5** (5%). The second half of the original solution was allowed to stand an additional 24 hours before treatment with excess methyl iodide. Analysis indicated the ratio of **13** to **5** was 90:10.

Benzoylation of Tetramethylammonium 1-Mercapto-2-methylmercaptofumaronitrile.—A solution of benzoyl chloride (0.032 g., 0.00023 mole) and the tetramethylammonium salt of *trans*-**14** (0.050 g., 0.00022 mole) in tetrahydrofuran (0.5 ml.) and methanol (3 ml.) was allowed to stand for 3 hours and was then evaporated *in vacuo*. From an ether extract of the residue there was obtained a semi-solid which was recrystallized from methylcyclohexane–ether at −40°. The infrared spectrum of the crystalline product (0.04 g., 70%), m.p. 71–73°, was identical with that of previously prepared *trans*-**17**.

Cleavage of Disodium *cis-cis*-9 with Potassium Borohydride.—To a stirred suspension of potassium borohydride (0.040 g., 0.00073 mole) in tetrahydrofuran (3 ml.) and methanol (2 ml.) there was added in one portion disodium *cis*-*cis*-**9** (0.10 g., 0.00031 mole). After 3 minutes methyl iodide (0.5 g.) was added and the mixture was evaporated *in vacuo*. From a methylene chloride extract of the residue there was obtained on concentration 0.06 g. (58%) of a yellow crystalline solid whose infrared spectrum was identical to that of pure *cis*-**5**. No trace of *trans*-**13** was detected.

Cleavage of Disodium *trans-trans*-10 with Potassium Borohydride.—A suspension of potassium borohydride (0.077 g., 0.00145 mole) in methanol (8 ml.) was added over 15 seconds to a solution of disodium *trans*-*trans*-**10** (0.190 g., 0.000590 mole) in tetrahydrofuran (4 ml.). After 5 minutes methyl iodide (0.5 ml.) was added, and 10 minutes later the solution was evaporated *in vacuo* to a dry residue which was extracted with methylene chloride. Evaporation of the extract *in vacuo* gave 0.173 g. (87%) of a yellow crystalline solid. Quantitative infrared analysis of a methylene chloride solution of the product employing the 6.60 and 12.25 μ bands indicated that the ratio of *trans*-**13** to *cis*-**5** was 6.7:1.

The same experiment was repeated employing DME as solvent. The yield of mixed isomers was 78% and the *trans*:*cis* ratio was 4.4:1.

Reductive Cleavage of *cis-cis*-11.—In the studies of reductive cleavage reactions of *cis*-*cis*-**11** and *trans*-*trans*-**12** various reducing agents were employed and the stereochemistry of the cleavage products was determined by preparing derivatives of the fragments. Such factors as order of addition, rate of addition and solvent were found to play a major role in determining the ratio of *cis*/*trans* isomers after cleavage and during methylation.

A. Potassium Iodide.—Iodine was liberated rapidly from a mixture of *cis*-*cis*-**11** (0.189 g., 0.00610 mole), powdered potassium iodide (0.204 g., 0.00123 mole) and methyl iodide (0.200 g., 0.00141 mole) in DME (8 ml.) which was stirred for 30 minutes at 25°. The mixture was diluted with methylene chloride, washed with dilute sodium bisulfite solution and with water and was dried. Evaporation of the solvent gave 0.184 (89%) of a yellow crystalline solid. Infrared spectral analysis using the 6.60 and 12.25 μ bands showed the ratio of *cis*-**5**:*trans*-**13** was 5.7:1.

B. Potassium Borohydride.—A solution of *cis-cis*-**11** (0.170 g., 0.00055 mole) in tetrahydrofuran (6 ml.) was cooled to 0° and stirred while a suspension of potassium borohydride (0.07 g., 0.0013 mole) in methanol (12 ml.) was added over 5 seconds. After 1 minute excess methyl iodide (1.5 ml.) was added and the reaction mixture was evaporated to dryness *in vacuo*. The residue was extracted with methylene chloride and the extract was decolorized and evaporated. There was obtained 0.157 g. (85%) of pure *cis*-**5**. None of the *trans* isomer could be detected spectrally.

C. Sodium Dithionite.—A suspension of *cis-cis*-**11** (0.250 g., 0.00081 mole) in methanol (30 ml.) was treated at 0° with a solution of sodium dithionite (0.148 g., 0.00086 mole) in 0.9% sodium hydroxide solution (9 ml.). The mixture was stirred 15 minutes before an excess of methyl iodide (1.5 ml.) was added. After an additional 30 minutes, water and methylene chloride were added, and the organic layer was separated. From the dried extract there was obtained 0.215 g. (78%) of a crude product which contained 86% *cis*-**5** according to its infrared spectrum.

Reductive Cleavage of *trans-trans*-12. A. Potassium Iodide.—The procedure of A above was repeated employing *trans-trans*-**12** in the same amounts and under the same conditions. A high yield (>90%) of a mixture of *cis*-**5** and *trans*-**13** was obtained in the ratio 3.42:1.

B. Potassium Borohydride.—The procedure of B was repeated employing *trans-trans*-**12** in the same amounts and under the same conditions. There was obtained 0.163 g. (81%) of a mixture of *cis*-**5** and *trans*-**13** in the ratio 1.65:1.

Repetition of this experiment employing DME as solvent gave an 83% yield of *cis*-**5** and *trans*-**13** in the ratio 1:1.91.

C. Sodium Dithionite.—The procedure of C above was repeated employing *trans-trans*-**12** in the same amounts and under the same conditions. There was obtained 0.217 g. (79%) of a mixture of *cis*-**5** and *trans*-**13** in the ratio 1:7.55.

Thermal Equilibration of *cis*-5 and *trans*-13.—Small samples (0.1 g.) of pure *cis*-**5** and *trans*-**13** were placed in clean Pyrex tubes which were flushed thoroughly with nitrogen before sealing. The tubes were completely immersed in the dark in an oil-bath whose temperature could be controlled. The tubes were removed and cooled quickly, and the crystallized contents were analyzed by infrared spectral analysis on the basis of previously calibrated spectra from known mixtures. The extent of decomposition was negligible in all runs. At 250° after 2 hours, equilibrium had been reached. The tubes containing *cis*-**5** and *trans*-**13** originally showed final compositions of [**5**]/[**13**] = 1.63 and 1.94, respectively. Identical runs were carried out in which to each tube was added a tiny crystal of iodine. The [**5**]/[**13**] ratios in these cases were 1.86 and 1.94, respectively. Similar experiments with iodine were carried out at 157° (43 hours) and 191° (9 hours). The equilibrium constants at these temperatures were determined to be 2.39 and 2.08, respectively.

Influence of Solvent and Cation on Thiacyanocarbon Anion Stability.—The studies made in Table I were in general carried out by dissolving the salt in the oxygen-free solvent and following changes by periodically recording the ultraviolet spectra. In some cases solvents were removed and analyses performed by quantitative infrared analysis. In others the solutions were methylated, and the methylation products were analyzed spectrally. Because of differences in the accuracy of the various analytical procedures, some of the percentages may be in error by as much as 10%. For this reason the results in the table reflect the configurational stability of the various anions only semi-quantitatively.

Ultraviolet Light-induced Isomerization of *trans*-13 to *cis*-5.—A solution of *trans*-**13** (0.50 g., 0.0029 mole) in methanol (50 ml.) was heated at reflux under nitrogen, and the flask was irradiated by a broad spectrum ultraviolet source for 12 hours. The solvent was removed *in vacuo* to give 0.5 g. (100%) of a yellow crystalline product whose infrared spectrum showed it to be essentially pure *cis*-**5**. Only traces of *trans*-**13** could be detected.

Ultraviolet Light-induced Isomerization of *cis*-3 and *trans*-16.—Disodium *trans*-**16** (0.300 g., 0.00161 mole) was placed in a Pyrex polymer-tube and purged with dry nitrogen overnight. Deoxygenated water (15 ml.) was added and the tube was sealed under a partial vacuum. The tube was irradiated for 21 hours with a broad spectrum ultraviolet source, and the temperature in the tube remained at 55° during this period. The tube was cooled, and the visible spectrum of the solution was recorded. It was previously established that Beer's law holds for the absorption bands at 366 mμ in *cis*-**3** and 402 mμ in *trans*-**16** in aqueous solutions of mixtures of **3** and **16**. Analysis in this manner indicated that the composition of the solution after irradiation was 27.4% *cis*-**3** and 72.6% *trans*-**16**. The photochemical steady-state *cis*/*trans* ratio is 0.38.

Under the identical conditions disodium *cis*-**3** was employed as starting material, and the *cis*/*trans* ratio after irradiation was determined to be 0.36 at 55°. Also, infrared analysis of the salt mixtures in the two experiments showed them to be indistinguishable. A portion of the solution from both runs was methylated with excess methyl iodide and the resulting dimethyl derivatives were analyzed by the infrared method. It was determined only that the *trans* isomer predominated.

When these experiments were repeated with the bis-(tetramethylammonium) salt corresponding to *trans*-**16**, the same *cis*/*trans* steady-state ratio was observed within the limits of experimental error. Irradiation of the corresponding *cis* isomer curiously led to extensive decomposition.

Furthermore, it was determined that degassed aqueous solutions of disodium *trans*-**16** were completely stable to isomerization over 5 days in diffuse laboratory light. However, under the same conditions bis-(tetramethylammonium) *trans*-**16** isomerized to the *cis* isomer to the extent of 29%.

Ultraviolet irradiation of disodium *cis*-**3** in ethanol at 40° for 10 hours gave a mixture of *cis*-**3** and *trans*-**16** in the ratio 1:3.35. Beginning with disodium *trans*-**16** and with bis-(tetramethylammonium) *trans*-**16**, the corresponding ratios were 1:2.85 and 1:1.94, respectively.