Thiacyanocarbons. 6. 1,4-Dithiino[2,3-*c*;6,5-*c'*]diisothiazole-3,7-dicarbonitrile, Isothiazole[3,4-*f*][1,2,3,4,5]pentathiepine-8-carbonitrile, and Disodium 5-Cyanoisothiazoledithiolate†

S. A. Vladuchick,* T. Fukunaga,* H. E. Simmons, and O. W. Webster

E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

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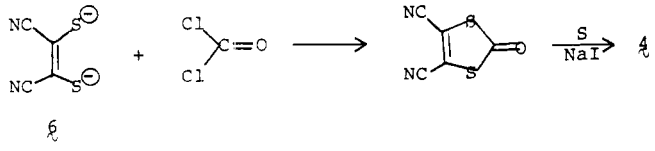
The synthesis of 1,4-dithiino[2,3-*c*;6,5-*c'*]diisothiazole-3,7-dicarbonitrile and isothiazole[3,4-*f*][1,2,3,4,5]pentathiepine-8-carbonitrile by a sulfur insertion–rearrangement reaction of 1,4-dithiin-2,3,5,6-tetracarbonitrile is described. The sulfur insertion–rearrangement of disodium dimercaptomaleonitrile gives 5-cyanoisothiazoledithiolate. The physical and chemical properties of these heterocyclic systems are reported together with a qualitative molecular orbital treatment which provides the key to understanding their properties.

Thiacyanocarbons[1] are an interesting class of compounds in that they can be prepared entirely from inorganic sources, namely, sodium cyanide, carbon disulfide, and sulfur. Their versatility as intermediates for the synthesis of novel heterocycles has been demonstrated.[1,2] Heterocycles reported previously[1] include stable tetracyano-1,4-dithiin (**1**) and tricyano-1,4-dithiino[*c*]isothiazole (**2**), both of which contain $4n$ cyclic π electrons. The isothiazole **2** was obtained from **1** by a sulfur insertion–rearrangement reaction as shown in Scheme I. The ring opening to give the *trans*-dicyanoethylene intermediate **3**[1] is assisted by resonance stabilization of the sulfide anion portion of the intermediate. This unusual reaction has now been extended to the synthesis of dicyano-1,4-dithiino[2,3-*c*;6,5-*c'*]diisothiazole **4**[3] and 5-cyanoisothiazole dithiolate **7**.[4,5] We report here the synthesis and properties of these molecules together with a qualitative molecular orbital (MO) treatment which provides the key to understanding their properties.

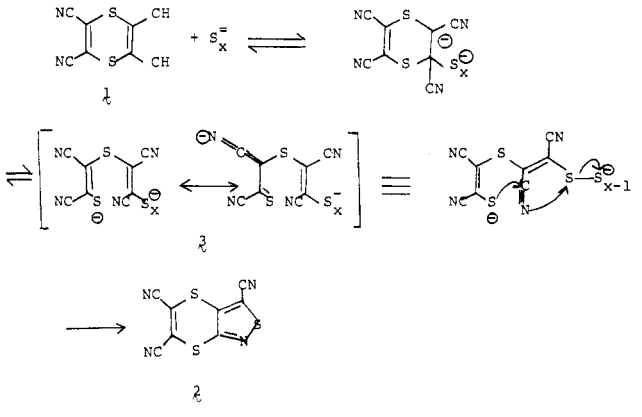
Synthesis

The reaction of **1** with sulfur in the presence of a basic catalyst, such as sodium iodide or tertiary amines, affords **4** as a pale yellow crystalline solid, mp 286–289 °C. The isothiazole **2** is most probably an intermediate to **4** (Scheme II). Application of the sulfur insertion–rearrangement mechanism discussed above predicts that the negatively charged sulfur nucleophile adds to **2** followed by ring opening to give preferentially **5a** which is better stabilized than the alternative intermediate **5b**. The former can cyclize to give **4**. The trans geometry of **4** has been unambiguously established by three-dimensional, single-crystal, X-ray analyses.[6] We find no evidence for the presence of the cis isomer which would have been derived from **5b**. Compound **4** is prepared more conveniently in the laboratory from disodium dimercaptomaleonitrile (**6**, Bähr's salt[7]) via 4,5-dicyano-1,3-dithia-2-oxocyclopentene.[8] Polysulfide, generated from sulfur and a base, is again a useful catalyst for conversion to **4**.

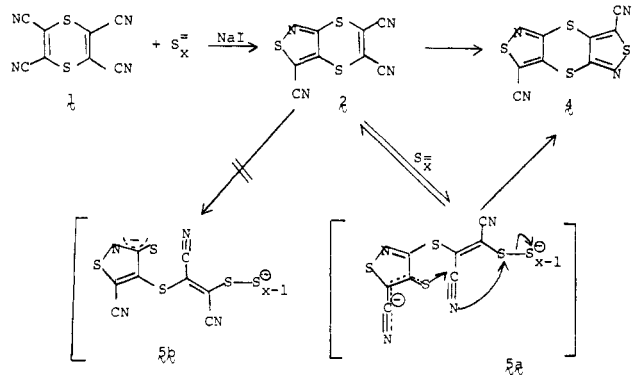


Bähr's salt, **6**,[7] itself undergoes a formal sulfur insertion–rearrangement reaction to give the isothiazole **7** (Scheme III).[9] The reaction proceeds slowly in ethanol with nucleophilic catalysts; however, it is greatly accelerated by addition of a small amount of **1**. This result

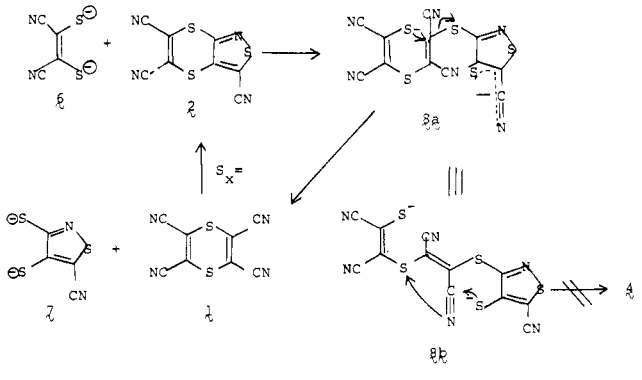
Scheme I. Sulfur Insertion–Rearrangement Reaction



Scheme II



Scheme III



† Contribution No. 2652.

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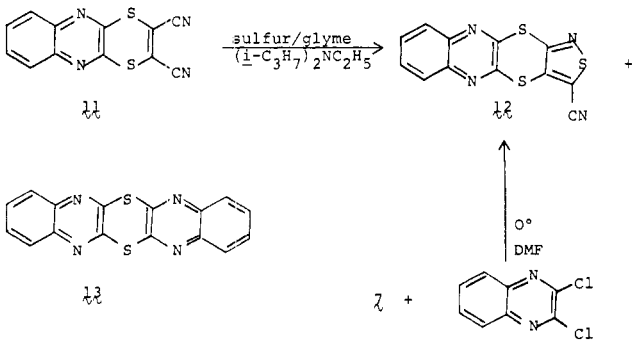
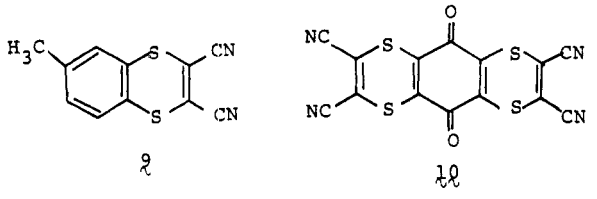
Scheme IV



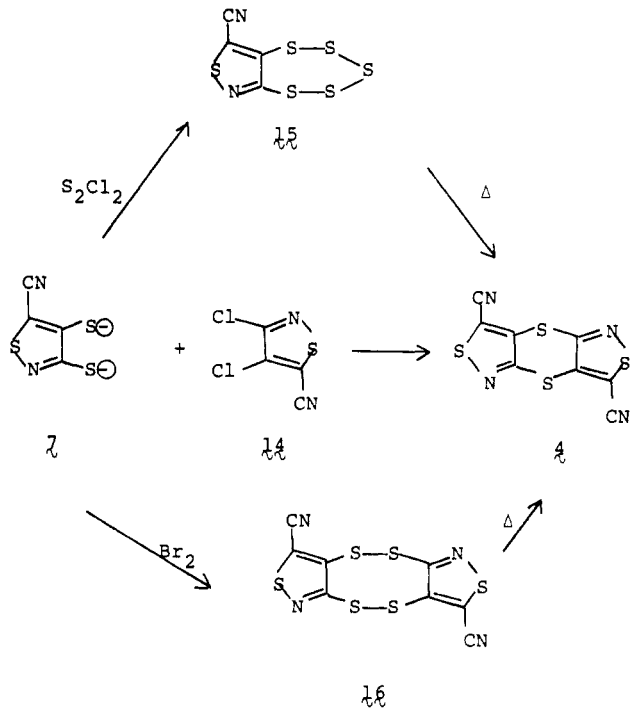
suggests that the key step is reaction of **6** with **2**, which is generated in situ from **1** as discussed in Scheme I. The ring-opened intermediate **8** does not possess a good leaving group to assist ring closure to form **4** (see **8b**); instead, it undergoes a sulfide exchange reaction (see **8a**) to give **7** and to regenerate the catalyst **1**.

In the absence of electron-withdrawing groups capable of stabilizing the ring-opened sulfide intermediate, the dithiodicyanoethylene–isothiazole rearrangement does not take place. For example, 6-methyl-2,3-dicyanobenzodithiin (**9**) is inert to polysulfide ion. The reaction of **10**[10] with

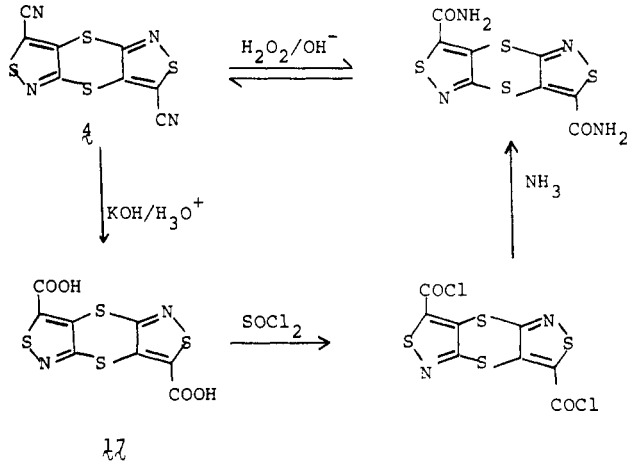


sulfur and base does not give the rearranged isothiazole. However, **10** is reduced to the corresponding hydroquinone. Similar treatment of 2,3-dicyanoquinoxalodithiin **11**[11] (prepared from quinoxaline-2,3-dithiol and dichloromaleonitrile[12]) gives only small amounts of the isothiazole **12** (Scheme IV). The main product **13**[13] results from disproportionation of **11**. The isothiazole **12** is, however, obtained by the reaction of **7** with 2,3-dichloroquinoxaline in DMF at 0 °C in good yield. A variety of ortho-substituted aromatic dihalides react with **7**. For example, **7** reacts with 3,4-dichloro-5-cyanoisothiazole (**14**)[14] to give **4** (Scheme V). This conversion provides an additional confirmation for the structure **7**. Sulfur dichloride also reacts with **7** to produce the novel isothiazolo[3,4-*f*]-[1,2,3,4,5]pentathiepine-8-carbonitrile (**15**).[15] Neither the

Scheme V



Scheme VI



source of the additional sulfur nor the mechanism of the formation of **15** has been investigated. Pentathiepine **15**, a pale yellow solid, is stable in acid but degrades in base. Pyrolysis of **15** gives **4**. Single-crystal X-ray analysis[16] of **15** unambiguously confirms the structure assignment in which the C_2S_5 ring exists in the chair conformation. The chemistry of this novel ring system (**15**) and additional coupling reactions of **7** with various vicinal dihalides will be reported in separate papers.

Finally, the oxidation of **7** with bromine, iodine, or H_2O_2 gives **16**[17] which extrudes sulfur at 210 °C to form **4**.

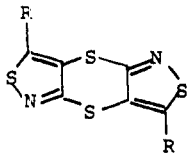
Properties

Dicyanodithiinodiisothiazole **4** is a remarkably stable dithiin derivative. Unlike most dithiins, **4** does not extrude

(1) (a) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962); (b) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *ibid.*, *84*, 4756, 4772, 4782 (1962).
(2) H. E. Simmons, R. D. Vest, S. A. Vladuchick, and O. W. Webster, *J. Org. Chem.*, previous paper in this issue.
(3) S. A. Vladuchick, U.S. Patent 4 067 879 (1978).
(4) S. A. Vladuchick, U.S. Patent 4 066 656 (1978).
(5) S. A. Vladuchick, U.S. Patent 4 110 335 (1978).
(6) L. J. Guggenberger and S. A. Vladuchick, *Acta Crystallogr.*, in press.
(7) G. Bähr and G. Schleitzer, *Chem. Ber.*, **88**, 1771 (1955); *90*, 438 (1957); G. Bähr, *Angew. Chem.*, **68**, 525 (1956).
(8) C. G. Krespan, U.S. Patent 3 140 295 (1964).
(9) R. D. Vest, U.S. Patent 3 197 472 (1965). This patent describes a salt of **5** as the coproduct of the reaction of **2** with potassium dimethyldithiocarbamate. This coproduct, however, was not further identified or characterized.
(10) K. Fickentscher, *Arch. Pharm. Ber. Dtsch. Pharm.*, **302**, 285 (1969).
(11) H. Saikachi and S. Tagami, *Yakugaku Zasshi*, **82**, 1312 (1962); *Chem. Abstr.*, **59**, 1635c (1963).
(12) E. L. Martin, U.S. Patent 3 070 622 (1962).
(13) L. Wojciechowski, Polish Patent 64 713 (1972); *Chem. Abstr.*, **79**, 6780*g* (1973).
(14) E. A. Mailey, U.S. Patent 3 341 547 (1967).
(15) S. A. Vladuchick, U.S. Patent 4 094 985 (1978).
(16) Crystal data: monoclinic, space group $P2_1/c$; at 26 °C, a = 16.722 (14) Å, b = 6.240 (5) Å, c = 9.249 (5) Å, β = 104.49 (5)°. The pentathiepine ring adopts a chair conformation with S–S bond distances which range from 2.051 (1) to 2.063 (1) Å. Details of the structure will be submitted for publication in *J. Org. Chem.* by R. L. Harlow and W. K. Moberg.
(17) The antistereochemical assignment is tentative.

sulfur on heating. The tricyclic ring skeleton, while it contains 16 π electrons, is retained throughout the hydrolysis and subsequent transformations. Saponification of **4** followed by acidification gives the bright primrose yellow dicarboxylic acid **17** (Scheme VI). The diacid forms colorless crystalline complexes solvated with tetrahydrofuran or dimethylformamide. Removal of the solvents yields bright yellow powders of **17**. X-ray analysis[18] shows the trans structure as in **4**. The molecular structure, however, is quite unusual for a dithiin derivative[19] in that it is planar and forms infinite chains by hydrogen bonding through the carboxylic acid groups. In the crystal lattice, the molecules are very tightly packed. The perpendicular distance between adjacent molecules, 3.41 Å, is very short and nearly identical with the van der Waals distance of benzene. In contrast, the pale yellow dinitrile **4**, like all other dithiins, is nonplanar and folded along the dithiin S–S axis by a dihedral angle of 144.9°.[6] These observations, together with SCF–LCAO–MO–CI calculations[20] discussed later, suggest that the bright yellow color of **17** is caused by intermolecular interactions unique to the solid.

The diacid **17** decarboxylates readily in boiling dimethylformamide (DMF) or diglyme at a temperature considerably below the decomposition temperature (250 °C) of the solid to give **18**. The parent compound **18** can

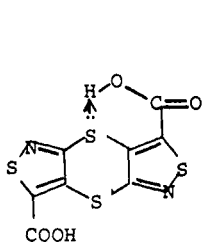


	R		R
18	H	**22**	NH_2
19	$COOCH_3$	**23**	$NHCOOC(CH_3)_3$
20	CON_3	**24**	$NHCOCH_3$
21	COC_6H_5	**25**	$NHCOOCH_2C_6H_5$

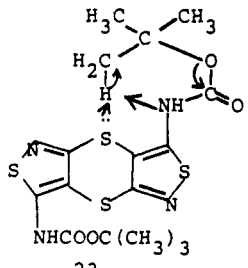
be obtained directly and more conveniently from **4** by hydrolytic decarboxylation in sulfuric acid at 180 °C.

The diacid **17** is convertible to the diacid chloride, to diesters, to diamides, and to the dicarboxazide (**20**) by standard methods and to the benzoyl derivative (**21**) by a Friedel–Crafts reaction. Reaction of the methyl ester **19** with phenylhydrazine in boiling DMF gives the parent **18**; however, in the absence of phenylhydrazine, **19** is entirely stable.

Thermal decomposition of the carboxazide **20** in *p*-xylene containing *tert*-butyl alcohol gives the diamine **22** directly and cleanly in 80–95% yield when the reaction temperature is raised above 130 °C by slowly distilling off the *tert*-butyl alcohol. Nearly 6 mol of gas ($2\ N_2 + 2\ C_4H_8 + 2\ CO_2$) evolve per mole of **20**. Below 100 °C, a mixture of the diamine **22** and intermediate *tert*-butylurethane **23** is obtained. In the absence of *tert*-butyl alcohol, only intractable red polymeric isocyanate is formed. The facile thermal decomposition of **23** and decarboxylation of **17** are suggestive of the dithiin sulfur assistance depicted.



17

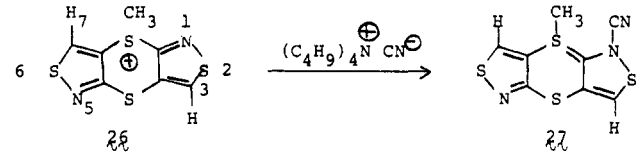


23

Diamine **22** is a stable, pale yellow solid, but pure samples are difficult to obtain except by this method. For example, hydrolyses of the acetamide **24** and benzylurethane **25** obtained by the rearrangements of **20** in acetic anhydride and benzyl alcohol, respectively, proceed only sluggishly, and the dark colored products are difficult to purify.

The dithiinodiisothiazole system is thus found to be stable regardless of the electronic nature of substituents (e.g., **4**, **17**, **18**, and **22**), although unusual substituent effects on stabilities are often observed in other cyclic $4n$-π-electron systems.[21]

Like typical isoxazole systems, parent isothiazole **18** is a weak base and forms a colorless hydrobromide, which regenerates **18** in alcohol. It is also a soft nucleophile and reacts with the Meerwein reagents to give the 4-alkyl sulfonium derivatives, for example, **26**. The structure assignment is based on its stability to hydrolysis[22,23] and on the comparison of ^1H NMR data (see Experimental Section) with those of *N*-methyl-2,1-benzisothiazolium[24] and 10-methylphenoxathiinium salts[23] as well as the ^{13}C NMR comparison of **26** and **18**. Treatment of **26** with



26 **27**

cyanide ion gives a colorless stable ylide **27** that shows (besides ν (C≡N) at 2220 cm^{-1}) characteristic absorptions at 1610 and 1540 cm^{-1}. The ^1H and ^{13}C NMR show neither protons attached to sp^3 carbon nor the presence of sp^3 carbon, except methyl. Whereas the isothiazole protons and the 3- and 7-carbons of **26** appear as closely spaced pairs ($\Delta\delta$ = 0.03 and 2.28 ppm, respectively) in the NMR, they are separated by 1.42 and 16.7 ppm in **27**. The chemical shifts of the lower field resonances are similar to the corresponding shifts of **26**. On these bases, the novel structure **27** is assigned to the ylide. Similar ylides (ν 1610 and 1540 cm^{-1}) appear to form also with methoxide anion and hydrazine.

Oxidations of the dithiinodiisothiazole system parallel those of dithiins and thianthracenes.[19,25] Thus, an intensely blue solution of the radical cation of **4** is obtained when a concentrated sulfuric acid solution of **4** is treated with concentrated nitric acid. ESR spectral analysis[26]

(18) G. Teufer, P. Gilmour, L. J. Guggenberger, to be submitted for publication in *Acta Crystallogr.*

(19) (a) D. S. Breslow and H. Skolnik, "The Chemistry of Heterocyclic Compounds: Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles", Interscience, New York, 1966, Part II, p 112. (b) A. R. Katritzky, Ed., "Physical Methods in Heterocyclic Chemistry", Vol. V, Academic Press, New York, 1972, and references therein.

(20) The authors thank Dr. M. D. Gordon of the Chemicals, Dyes, and and Pigments Department for developing parameters for and running PPP calculations.

(21) For example, see D. Farquhar and Leaver, *Chem. Commun.*, 24 (1969).

(22) *N*-Alkyl-2,1-benzisothiazolium salts rapidly decompose in acid or base, yielding *o*-aminobenzaldehydes: M. Davis, E. Homfeld, and K. S. Lal Srivastava, *J. Chem. Soc., Perkin Trans. 1*, 1863 (1973).

(23) 10-Alkylphenoxathiinium salts are stable to hydrolysis: R. M. Acheson and J. K. Slubbs, *J. Chem. Soc., Perkin Trans. 1*, 899 (1972).

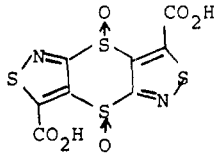
(24) M. Davis, L. W. Deady, and E. Homfeld, *J. Heterocycl. Chem.*, 14, 1011 (1974).

(25) P. D. Sullivan, *J. Am. Chem. Soc.*, **90**, 3618 (1968); Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

(26) The authors thank Dr. P. J. Krusic of this department for obtaining and interpreting ESR spectra.

shows an expected five-line spectrum. Each line is further resolved partially into five lines. To our knowledge, this represents the first example of a radical cation bearing cyano groups.

Similarly, diacid **17** also forms a bright lime-colored solution which slowly precipitates the 4,8-disulfoxide dicarboxylic acid **28**. In Me_2SO, **28** exothermically decarboxylates to **29**. The disulfoxide **29**, however, is obtained more cleanly by treatment of **18** with sodium nitrate in HF. Oxidation of **18** with trimethylsilyl nitrate, on the other hand, stops cleanly at the monosulfoxide **30**. Hypochlorite oxidation of the dicarboxylic acid **17** proceeds with gas evolution at 70 °C to give the 4-sulfoxide 8-sulfone **31**.



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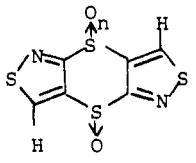


29 n = 1

30 n = 0

31 n = 2

Discussion

Cyclic conjugated systems having negative resonance energies (RE) are often claimed to be highly unstable and are termed antiaromatic. Cyclic $4n$-π-electron systems generally belong to this class, and the molecules often exist in nonplanar and/or bond-alternating structures in order to avoid the resonance destabilization. The highly unstable nature of these compounds has been thus alleged to be of thermodynamic origin. We have found, however, that the kinetic criterion expressed in terms of the energy gap between the frontier orbitals (highest occupied, HO; lowest unoccupied, LU) is an alternative and more reliable measure for assessing the apparent stability (e.g., isolability) of these compounds. This analysis[27] is particularly useful if the delocalized state is the ground state or is thermally populated.

p-Dithiin, *p*-dioxin, and their derivatives are generally readily isolable and much more stable than might be expected for potentially antiaromatic $4n$-π-electron systems. *p*-Dioxin is found to be planar.[28] Although *p*-dithiin and thianthrene[19] exist in boat conformations in the solid state, they appear to oscillate rapidly in solutions via planar forms. In the solid, dinitrile **4** is puckered, and diacid **17** is planar. The X-ray data indicate that the dithiin ring is more delocalized in **17** than in **4**;[6,18] the C–S bonds (1.741 Å) of **17** are shorter and the C–C bonds (1.432 Å) are longer than the corresponding bonds (1.755 and 1.415 Å, respectively) of **4**.[6,18,29] The C–C bonds of **17** are very similar, perhaps fortuitously, to the corresponding bonds in anthracene (1.436 Å). We have failed to observe the presence of the diastereomeric pairs of the optically active (+)-α-methylbenzylamide and (−)-2-octanol ester of **17** by NMR and were also unsuccessful in resolving the diastereomers. Thus, in solutions the ring system is either planar or rapidly oscillating between two boat forms.

(27) A compound having a large HOMO–LUMO gap and a bonding HOMO is expected to be stable and isolable regardless of the resonance energy. The threshold gap is approximately 0.35β by HMO calculations. For small systems slightly larger gaps are required. A full account of this analysis will be reported in a forthcoming paper.

(28) R. C. Lord and T. C. Rounds, *J. Chem. Phys.*, **58**, 4344 (1973); J. E. Beach, *ibid.*, **9**, 54 (1941).

(29) The bonding characteristics of the isothiazole rings are very similar in both structures; see ref 6 and 18.

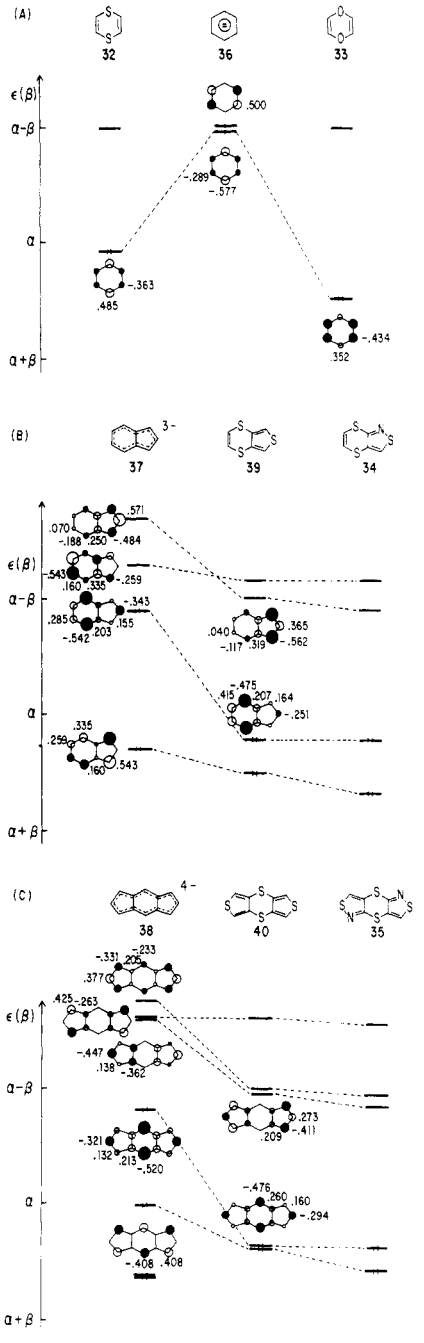


Figure 1. Hückel frontier molecular orbitals of (A) dithiin and dioxin, (B) dithiinoisothiazole, and (C) dithiinodiisothiazole. The energy unit is β. The sizes of the open and filled circles in the orbital figures reflect the phase changes and are roughly proportional to the coefficient at the position (see ref 30 for parameters).

Table I. HMO Frontier Molecular Orbital Energies (β)

compd	LUMO	HOMO	gap
36	−1.000	−1.000	0
32	−1.000	0.078	1.078
33	−1.000	0.464	1.464
37	−1.295	−0.902	0.393
39	−1.015	0.208	1.224
34	−0.911	0.212	1.123
38	−1.618	−0.820	0.798
40	−0.967	0.356	1.323
35	−0.861	0.361	1.223

LCAO-MO Treatment

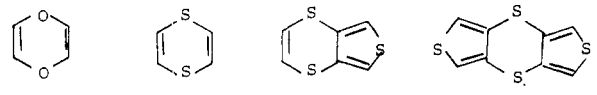
Isostructural and isoelectronic hydrocarbons corresponding to *p*-dithiin **32**, *p*-dioxin **33**, dithiinoisothiazole **34**, and dithiinodiisothiazole **35** are the antiaromatic

benzene dianion **36**, indene trianion **37**, and *s*-indacene tetraanion **38**, respectively. Hückel MO (HMO) calculations[30] (Figure 1, Table I) show that the hydrocarbon anions have highly antibonding HOMO's and small HOMO–LUMO gaps (in the benzene dianion the HOMO and LUMO are degenerated), contributing to the thermodynamic and kinetic instability, respectively.[27]

Inspection of the frontier MO (FMO) diagrams of the anions (Figure 1) show that coefficients at the sites where sulfur replacements are to be implemented are large in the HOMO's and zero or very small in the LUMO's. Replacement of a carbanionic center by a more electronegative neutral sulfur atom lowers the MO energies. The extent of the stabilization ($\Delta\epsilon_i$) of a given MO is qualitatively proportional[31,32] to the square of the coefficient, $C_{i,r}$, of the MO at the replacement site r (eq 1), where $\Delta\alpha_r$ is

$$\Delta\epsilon_i \simeq C_{i,r}^2 \Delta\alpha_r \quad (1)$$

the difference in the Coulomb integrals between the hetero atoms and the carbon atoms. Thus, the HOMO's of the anions are expected to be greatly stabilized by sulfur replacements, whereas the LUMO energies are only slightly affected. As shown in Figure 1, *p*-dithiin **32** and *p*-dithiinothiophenes **39** and **40** as well as *p*-dioxin **33** no longer have occupied antibonding MO's, and, more importantly, they all have large HOMO–LUMO gaps. It should be noted that the relative ordering of the LUMO and the next LUMO (NLUMO) is reversed in going from **37** to **39**. The reason for this is that coefficients at the replacement sites of **37** and, therefore, the stabilizing effects are much larger for the NLUMO than for the LUMO. The MO diagrams of **32**, **33**, **39**, and **40** have relatively bonding HOMO's and



	33	**32**	**39**	**40**
REPE (β)	+.014	-.017	-.0004	+.006

large HOMO–LUMO gaps and are typical for stable and isolable π-electron systems. However, resonance energies per π-electron (REPE) calculated according to the Hess–Schaad method[33] indicate that they are electronically essentially nonaromatic or antiaromatic. Thus, the stable and isolable systems **32** and **33** should be viewed as kinetically stable but thermodynamically anti- or nonaromatic species. Furthermore, unknown **39** and **40** are expected to be stable and isolable.[27] The essential feature in stabilizing these compounds is the placement of electronegative heteroatoms at *strategic* sites to increase the kinetic stabilities. Heteroatoms must be placed at such positions so that the HOMO is stabilized preferentially without significantly lowering the LUMO energies.

Effects of nitrogen introduction into **39** and **40** can be assessed in a similar manner. However, the Coulomb integral difference, $\Delta\alpha_r$, between carbon and sp^2 nitrogen is much smaller than that between carbon and divalent sulfur;[30] therefore, nitrogen introduction can be regarded as a minor perturbation.[32]

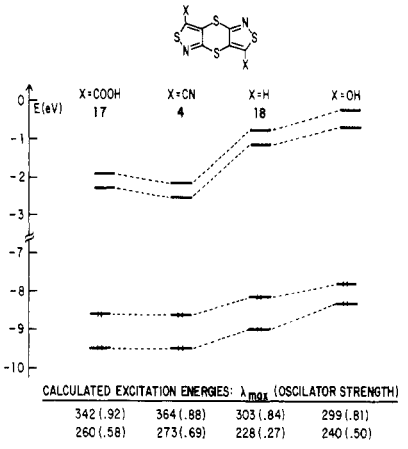


Figure 2. Pariser–Parr–Pople molecular orbitals of dithiinodithiazoles. Standard bond lengths were used: C=C, 1.380; C=N, 1.340; C—C, 1.435; C—S, 1.740; N—S, 1.640; C≡N, 1.163; C—CN, 1.450; C—COOH, 1.450.

Perturbation treatment of substituent effects within the HMO framework is useful only in assessing qualitative trends of MO energy changes. In principle, the effects can be treated as a combination of inductive and π-conjugative effects.[32] The former arises because substituents alter the effective Coulomb integrals of ring atoms. The π-conjugative effect is significant only for the MO's which lie energetically in close proximity with the MO's of the substituent. The effect is also proportional to the magnitude of the atomic coefficient at the substitution site.[32] Substituents such as COR and CN are inductively electron withdrawing and characteristically possess low-lying unoccupied MO's (conjugatively electron withdrawing). Thus, these substituents on the isothiazole rings of **34** and **35** stabilize the LUMO's much more than the HOMO's, and the HOMO–LUMO gaps may be substantially diminished. In fact, HMO calculations show that a carbonyl group on the isothiazole rings narrows the HOMO–LUMO gaps of **34** and **35** by approximately half ($\gtrsim 0.65\beta$). Cyano substituents on the dithiin ring of **34** should have little effect on the HOMO and LUMO energies (small coefficients). However, the NLUMO will be significantly stabilized by the substituent on the dithiin ring, and should become the LUMO of the 5,6-dicyano derivatives. The relatively low-lying LUMO's with large coefficients at the carbons bearing a cyano group are responsible for the facile ring opening of **1** and **2** by nucleophiles, e.g., eq 2 and 3.

$$1 \xrightarrow{S^{2-}} 2 \xrightarrow{S^{2-}} 5 \quad (2)$$

$$2 + 7 \rightarrow 1 + 5 \quad (3)$$

The π-conjugative effect of two amino groups on **35**, on the other hand, should significantly raise the NHOMO by strong mixing with the high-lying occupied MO (lone pair) of the amino group. Although this effect will be slightly offset by the inductive effect, the amino derivatives are predicted to be highly electron-rich and strongly nucleophilic.

Pariser–Parr–Pople (PPP) LCAO–MO–CI calculations[20,34] (Figure 2) confirm the qualitative conclusions

(30) The authors thank Dr. F. A. Van Catledge of this department for obtaining the parameters based on the Hinze–Beveridge formula for SCF π-electron calculations: $h_S = 1.11$, $h_N = 0.51$, $k_{C-S} = 0.69$, $k_{C-N} = 1.02$, $k_{N-S} = 0.78$. This parameter is the data base for the interactive program HUCKEL now available for QCPE, Program No. 385.

(31) C. A. Coulson and H. C. Longuett-Higgins, *Proc. R. Soc. London, Ser. A*, **191**, 39 (1947).

(32) For a general discussion of the perturbation MO method, see: (a) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961; (b) E. Heilbronner and H. Bock, "The HMO Model and Its Application", Engl. ed., Wiley, New York, 1976; (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969; (d) L. Salem, "Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, 1966.

(33) B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971); **95**, 3907 (1973).

(34) (a) M. D. Gordon and J. F. Neumer, *J. Phys. Chem.*, **78**, 1868 (1974). (b) The PPP method used here calculates the HOMO energies of −8.8 and −6.6 eV for aniline and tetrathiafulvalene, respectively.

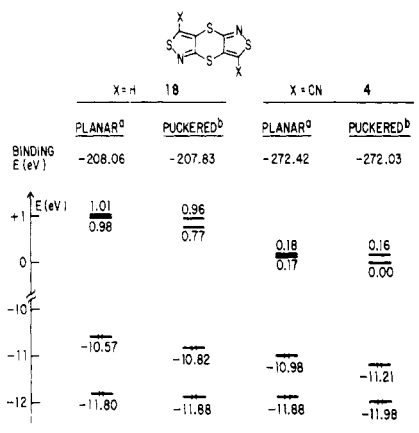


Figure 3. CNDO/2 calculations including sulfur 3d orbitals of planar and puckered dithiinodithiazoles 4 and 18. (a) The ring geometry of 17 (ref 18) is assumed. (b) The ring geometry of 4 (ref 3) is assumed.

discussed above. The electronic excitation energies calculated for 4 and 17 are in good agreement with the experimental spectral data in solution. Furthermore, the calculated excitation energies are found to vary little with the conformational changes of the dithiin rings. Since both planar and puckered molecules are predicted to be colorless or nearly colorless, intermolecular interactions in the crystal lattice are most likely responsible for the bright primrose yellow color of the solid diacid 17. The HOMO energies of 4, 17, and 18 (-8.6, -8.6, and -8.1 eV, respectively) are comparable to those of good electron donors.[34b] The expected low ionization potentials thus account for the formation of the radical cation of 4. Structures 18 and 22 are predicted to show even greater tendencies to donate electrons, but this has not yet been tested. The LUMO's of these compounds are highly antibonding as most electron donors are. The electron affinities are predicted to be between those of benzene and benzonitrile (E_{LUMO} = -0.98 and 2.5 eV, respectively).

CNDO/2 calculations[35] including sulfur d orbitals (Figure 3) were carried out for 4 and 18 with both planar and puckered geometries determined by X-ray analyses.[6,18] Although the X-ray data show that the planar dithiin ring is more delocalized than the puckered ring, the calculated binding energies and therefore the thermodynamic stabilities are essentially identical for the two forms.[36] The HOMO–LUMO gaps are large, and the FMO coefficients are similar in both forms. π-electron delocalization does not increase the thermodynamic stability of this ring system, and its thermal stability is better accounted for by the large HOMO–LUMO gap (kinetic stability).

Electron densities of the ring atoms are largest at the nitrogen atoms, whereas the dithiin sulfur has the largest coefficient in the HOMO. Soft electrophiles such as the Meerwein reagents and the oxidants we have used are expected to attack the central sulfur atoms of 18 (orbital controlled), while 18 may be protonated at the isothiazole nitrogen atom (charge controlled), forming the hydrogen bromide salt. The LUMO and NLUMO are nearly degenerate, and sulfur d orbitals contribute significantly. The atomic coefficients of these orbitals are well spread, and there is no obvious site for soft nucleophiles to attack. We have not been able to cleanly reduce, for example, 4, 17, and their derivatives by hydride reagents. Hard nucleophiles such as hydroxide anion attack the most positively charged site, for example, the nitrile carbon of 4, and lead to hydrolysis.

(35) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 44, 3289 (1966); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

(36) Since geometry optimizaitons were not performed, we cannot be certain of the relative stabilities of the two forms.

Conclusion

The novel heterocyclic system 1,4-dithiino[2,3-c;6,5-c']diisothiazole and related structures have been synthesized. The stabilities and reactivities of these cyclic π-electron systems can be best understood by analysis of the FMO and the HOMO–LUMO gaps by qualitative perturbation theory. The proposed relationship between the HOMO–LUMO gap and apparent kinetic stability is based on the principle of successive narrowing of the HOMO–LUMO level separation described by Fukui.[37]

Experimental Section

All melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam spectrometer using NaCl optics (2–15 μm) or on an Infracord spectrometer in Nujol mulls. Spectra were obtained from potassium bromide wafers. The visible and ultraviolet spectra were obtained by means of a Cary Model 11 recording spectrometer. 2,3-Quinoxalinedithiol was purchased from Eastman Organic Chemicals. 2,3-Dichloroquinoxaline and 3,4-dimercaptotoluene were purchased from Aldrich Chemical Co.

1,4-Dithiino[2,3-c;6,5-c']diisothiazole-3,7-dicarbonitrile (4). A mixture of 900 mL of 1,2-dimethoxyethane, sulfur (20.25 g, 0.633 mol), and sodium iodide (2.7 g, 0.018 mol) was heated at 80 °C under an atmosphere of nitrogen for 0.25 h. The suspension was cooled to room temperature, and 1,4-dithiin-2,3,5,6-tetracarbonitrile (1; 32.4 g, 0.15 mol) was added. The reaction mixture was heated under reflux for 20 h and cooled (-78 °C), and the crude product 4 (43.7 g, 100%) was separated by filtration. Recrystallization from toluene (using decolorizing carbon) gave pure 4: mp 286–289 °C; IR (KBr) 4.50 (s, CN), 6.78, 7.48, 7.78, 8.68, 10.43, 11.85, 12.30, 14.58, 14.98 μm; UV (CH_3CN) λ_{max} 338 nm (ϵ 10900), 278 (4950), 218 (25000); ^{13}C NMR (Me_2SO-d_6) 153.2, 133.0, 127.2, 108.3 ppm; mass spectrum, m/e 279.8988 (calcd for $C_8N_4S_4$, m/e 279.9006). Anal. Calcd for $C_8N_4S_4$: C, 34.3; N, 20.0; S, 45.7. Found: C, 34.6; N, 20.0; S, 45.4.

4 from 2-Oxo-4,5-dicyano-1,3-dithiacyclopentene. Sulfur (5.7 g, 0.18 mol) and sodium iodide (6.0 g, 0.04 mol) were heated at 80 °C under an atmosphere of nitrogen in 1,2-dimethoxyethane (500 mL) for 0.5 h. The solution was cooled to 50 °C, 2-oxo-4,5-dicyano-1,3-dithiacyclopentene[8] (30 g, 0.18 mol) was added, and the mixture was heated under reflux for 19 h. The suspension was cooled to 0 °C and the product 4 separated by filtration. Crude 4 (13.2 g, 53%) was identical with 4 prepared as described above.

Disodium 5-Cyanoisothiazoledithiolate (7). Bähr's salt (186 g, 1 mol), sulfur (40 g, 1.25 mol), 1,4-dithiin-2,3,5,6-tetracarbonitrile (21.6 g, 0.1 mol), and ethanol (2500 mL) were heated at 78.5 °C under an atmosphere of nitrogen for 3.5 h. The mixture was cooled and filtered to remove excess sulfur. The filtrate was evaporated to dryness under reduced pressure. Acetonitrile (1500 mL) was added to the residue, and the mixture heated gently at 50 °C for 1.5 h. The mixture was cooled and then filtered under an atmosphere of nitrogen. Crude 7 (102.5 g, 56%) was dried under vacuum and stored under N_2; mp 172–178 °C. Anal. Calcd for $C_4N_2S_3Na_2$: C, 22.0; N, 12.8. Found: C, 21.7; N, 13.1.

As 7 is difficult to purify, it was methylated, purified, and characterized as described below.

A portion of crude disodium 5-cyanoisothiazoledithiolate (7; 9.9 g, 0.045 mol) was methylated in methanol (500 mL) by using dimethyl sulfate (10 mL). Potassium carbonate (5.0 g) was added after 5 min of stirring, and the mixture was stirred at room temperature overnight. The suspension was filtered (solids discarded), and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in chlorobutane (400–500

(37) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, 42, 3399 (1969); K. Fukui, "Theory of Orientation and Stereoselection", Springer-Verlag, West Berlin and Heidelberg, 1970.

mL), and the inorganic salts were removed by filtration. The chlorobutane solution was treated with decolorizing carbon, filtered, and cooled to −80 °C. Colorless 3,4-bis(methylthio)isothiazole-5-carbonitrile (2.74 g, 83%) was isolated by filtration: mp 63.5–64.0 °C; UV (CH_3CN) λ_{max} 337 (ϵ 6360); ^1H NMR ($CDCl_3$, Me_4Si) δ 2.60–2.75 (d); ^{13}C NMR (CD_3CN, Me_4Si) 167.4, 137.5, 133.4, 110.96, 17.4, 14.3 ppm. Anal. Calcd for $C_6H_6N_2S_3$: C, 35.6; H, 3.0; N, 13.9. Found: C, 35.6; H, 3.2; N, 13.6.

6-Methylbenzodithiin-2,3-dicarbonitrile (9). 3,4-Dimercaptotoluene (5.0 g, 0.032 mol) was dissolved in cold dimethoxyethane (75 mL) and dichloromaleonitrile (4.7 g, 0.032 mol) added in one portion. Ethyldiisopropylamine (8.25 g) was added dropwise. The yellow suspension was stirred at room temperature overnight and filtered, and the filtrate was evaporated to dryness under reduced pressure. Recrystallization from benzene gave 4.9 g (67%) of **9**: mp 180–181 °C; NMR (C_6D_6) δ 1.6 (s), 6.4 (m), 6.45 (d); the IR was consistent with the structure; mass spectrum, *m/e* 229.9984 (calcd *m/e* 229.9972). Anal. Calcd for $C_{11}H_6N_2S_2$: C, 57.4; H, 2.6; N, 12.2; S, 27.8. Found: C, 57.4; H, 2.9; N, 12.1; S, 27.7.

Isothiazolo[3′,4′;2,3][1,4]dithiino[5,6-*b*]quinoxaline-3-carbonitrile (12). Dichloroquinoxaline (9.95 g, 0.05 mol) was dissolved in 100 mL of dimethylformamide and cooled to 0 °C. Disodium 5-cyanoisothiazoledithiolate (**7**) (10.9 g) was added in one portion. The mixture was stirred at 0 °C for 0.5 h and then poured into water, stirred, and filtered. The solids were rinsed with water. Crude **12** (5.59 g, 85%) was recrystallized from chlorobutane: mp 182–184 °C; IR (KBr) 4.5, 6.43, 6.61, 6.76, 7.69, 7.93, 8.48, 8.66, 8.83, 8.98, 9.80, 10.48, 11.98, 12.30, 13.24 μm. Anal. Calcd for $C_{12}H_4N_4S_3$: C, 48.0; H, 1.3; N, 18.7; S, 32.0. Found: C, 47.7; H, 1.6; N, 18.9; S, 32.3.

Isothiazolo[3,4-*f*][1,2,3,4,5]pentathiepine-8-carbonitrile (15). All glassware was dried by flaming under nitrogen. Disodium 5-cyanoisothiazoledithiolate (**7**; 32.4 g, 0.15 mol) was added to 2 L of 1,2-dimethoxyethane and cooled under an atmosphere of nitrogen to 0–5 °C with a methanol/ice bath. Sulfur monochloride (14 mL) in 1,2-dimethoxyethane (100 mL) was added slowly via an addition funnel, while the temperature was maintained at 5 °C. After the addition was complete, the suspension was allowed to warm to room temperature and then stirred for an additional 4 h. Inorganic solids were removed by filtration and discarded. The filtrate was evaporated to dryness under reduced pressure. Crude **15** (36.1 g, 98%) was purified by column chromatography with Mallenkrodt CC-7 Special and toluene/hexane eluent. Further purification by recrystallization from carbon tetrachloride gave analytically pure **15**: mp 143–144 °C; ^{13}C NMR (CS_2–$SiMe_4$–Me_2SO-d_6) 107.82, 139.1, 145.4, 170.1 ppm; mass spectrum, *m/e* 267.8447 (M^+; calcd for $C_4N_2S_6$, *m/e* 267.8386); the fragmentation pattern was consistent with the structure (stepwise loss of sulfur). Anal. Calcd for $C_4N_2S_6$: C, 17.9; N, 10.4; S, 71.7. Found: C, 18.1; N, 10.4; S, 71.9.

[1,2,5,6]Tetrathiocino[3,4-*c*;7,8-*c*′]diisothiazole-3,8-dicarbonitrile (16). Iodine (178 g, 0.7 mol) was added portionwise via Gooch tubing to a stirred suspension of disodium 5-cyanoisothiazoledithiolate (**7**; 153 g, 0.7 mol) in acetonitrile (2.5 L) under an atmosphere of nitrogen. The resulting suspension was stirred at room temperature overnight (~22 h) and filtered. The gray solid **16** (94 g, 78%) was washed well with water, methylene chloride, cyclohexene, acetonitrile, and ether: mp 252–254 °C; IR (KBr) 4.51, 6.89, 7.55 (w), 7.85 (br), 8.61 (w), 8.82, 10.54, 12.15, 12.54, 14.36 μm; the product analyzed for the monohydrate. Anal. Calcd for $C_8N_4S_6 \cdot H_2O$: C, 26.5; N, 15.5; S, 53.1. Found: C, 26.2; N, 15.2; S, 53.1.

Ion Radical of 1,4-Dithiino[2,3-*c*;6,5-*c*′]diisothiazole-3,7-dicarbonitrile. Compound **4** (1.0 g, 0.004 mol) was dissolved in cold, concentrated H_2SO_4 (10 mL). A cold 1:1 solution of concentrated H_2SO_4/HNO_3 was added dropwise until an intense blue color appeared. The solution was stable at 0 °C for about 0.75 h.

1,4-Dithiino[2,3-*c*;6,5-*c*′]diisothiazoledicarboxylic Acid (17). Compound **4** (19 g, 0.068 mol) was added to a solution of KOH (80 g, 1.43 mol) in H_2O (500 mL). Nitrogen was bubbled through the suspension while it was slowly heated to reflux. A rigorous nitrogen purge was continued to assist removal of generated ammonia. After 4–5 h, the pH of the exit gas was neutral. The suspension was cooled to room temperature and the dipotassium salt removed by filtration. The salt was dissolved in hot water, heated to 100 °C, and neutralized with 6 N HCl. On cooling, intensely yellow **17** was isolated: mp 230–247 °C; IR (KBr) 3.0-4.0 (br, H-bonded OH), 5.95 (s, carbonyl), 6.66 (s, conjugated C=C and/or C=N), 7.09, 7.50, 8.03 (s, CO), 10.29, 12.19, 14.05 μm. The mass spectrum of the silylated sample shows *m/e* 462 and 457, supporting presence of two carboxyl groups. A sample of **17** was recrystallized from THF (3 g/150 mL), and the colorless feathers were dried in vacuum to give an analytical sample as bright yellow powder: UV (EtOH) λ_{max} 368 nm (ϵ 11 700), 277 (4900), 219 (29 500). Anal. Calcd for $C_8H_2N_2S_4O_4$: C, 30.2; H, 0.6; N, 8.8; S, 40.3. Found: C, 30.4; H, 0.8; N, 8.6; S, 40.1.

Recrystallization of **17** from DMF gave DMF-solvated **17** as pale yellow feathers which were dried at 25 °C under vacuum and analyzed. Anal. Calcd for $C_8H_2N_2S_4O_4 \cdot 2DMF$: C, 36.2; H, 3.5; N, 12.1; S, 27.6. Found: C, 36.2; H, 3.5; N, 11.9; S, 28.0.

The potassium salt of **17** that precipitated from a dilute KOH solution of **17** upon addition of saturated KCl solution was recrystallized from water: UV (H_2O) λ_{max} 352 nm (ϵ 11 000), 272 (4000), 217 (32 300). Anal. Calcd for $C_8N_2S_4O_4K_2$: C, 24.4; N, 7.1; S, 32.5. Found: C, 24.5, 24.3; N, 7.3, 7.2; S, 32.4, 32.5.

The tetrabutylammonium salt was prepared from **17** and a 1 M methanolic solution of tetrabutylammonium hydroxide and recrystallized from acetone; mp 167–169 °C. Anal. Calcd for $C_{40}H_{72}N_4S_4O_4$: C, 60.0; H, 9.1; N, 7.0; S, 16.0. Found: C, 59.8; H, 9.0; N, 7.4; S, 15.8.

1,4-Dithiino[2,3-*c*;6,5-*c*′]diisothiazole (18). A mixture of **4** (4.6, 0.016 mol), concentrated sulfuric acid (125 mL), and water (50 mL) was heated at 180 °C for 3 h, at which time the solution was colorless. The solution was cooled to room temperature and poured over ice, and crude **18** was isolated by filtration. Recrystallization from chlorobutane gave 1.73 g (45%) of purified **18**: mp 190–191 °C; IR (KBr) 3.73 and 3.26 (s, =CH), 6.10 and 6.80, 7.59 (s), 7.75 (s), 11.85, 12.15, 12.35, 12.55, 12.78 μm; UV (CH_3CN) λ_{max} 295 (ϵ 11 500), 211 (17 900); ^1H NMR (Me_2SO-d_6) δ 9.08 (s); mass spectrum, *m/e* 229.9097 (calcd *m/e* 229.9101). Anal. Calcd for $C_6H_2N_2S_4$: C, 31.3; H, 0.9; N, 12.2; S, 55.7. Found: C, 31.4; H, 1.2; N, 12.3; S, 55.5.

Dihydrobromide of 18. To a solution of 2.3 g of **18** in 200 mL of acetic acid was added a solution of 5 mL of bromine in 20 mL of acetic acid at 60 °C. No bromine was taken up. After an induction period of about 1 h, a copious amount of HBr gas evolved, the bromine color faded, and solid precipitated. After being refluxed for 3 h, the mixture was cooled and filtered to give 3.70 g (94%) of the dihydrobromide as pale yellow solid, mp 212–216 °C dec. Anal. Calcd for $C_6H_4N_2S_4Br_2$: C, 18.4; H, 1.0; N, 7.1; S, 32.7. Found: C, 18.5; H, 1.0; N, 7.1; S, 32.7.

The dihydrobromide was also obtained in 89% yield by passing HBr gas into a boiling acetic acid solution of **18** for 30 min.

The dihydrobromide regenerated **18** when it was heated at 50 °C under vacuum or treated with water.

1,4-Dithiino[2,3-*c*;6,5-*c*′]diisothiazole-3,7-dicarbonyl Chloride (41). A mixture of **17** (64 g, 0.2 mol), thionyl chloride (900 mL), and dimethylformamide (15 mL) was heated under reflux for 6 h and cooled to room temperature; **41** (69 g, 71%) precipitated as an orange solid and was collected by filtration: mp 236–237 °C; IR (KBr) 5.84 (s, carbonyl), 6.84 (s, conjugated C=C and/or C=N), 7.45 (s), 7.55 (s), 7.75 (s), 7.85, 7.85, 8.50, 10.13, 10.54, 12.06, 14.2 μm; UV (CH_2Cl_2) λ_{max} 411 nm (ϵ 10 900), 301 (9380). Anal. Calcd for $C_8N_2S_4O_2Cl_2$: C, 27.1; N, 7.9; Cl, 20.0. Found: C, 27.1; N, 7.7; Cl, 19.9.

1,4-Dithiino[2,3-*c*;6,5-*c*′]diisothiazole-3,7-dicarbonyl Azide (20). A yellow suspension of **41** (7.1 g, 0.02 mol) in acetone (200 mL) was treated at 10 °C with a solution of sodium azide (2.8 g, 0.04 mol) in water (10 mL). The suspension was stirred for 4 h and crude **20** isolated by filtration. Azide **20** was washed with ice-cold water, acetone, and ether. Azide **20** (7.23 g, 98%) was isolated as a bright yellow solid: mp >100 °C dec; IR (KBr) 4.48, 4.58, 5.95 μm. The crude **20** was used for further transformations.

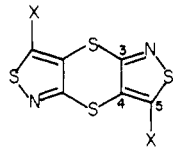
Rearrangements of 20. (a) Polymeric Isocynate. A suspension of 1.9 g of **20** in 100 mL of *p*-xylene was heated at 135 °C until gas evolution ceased. The dark orange mixture was cooled, filtered, and washed with toluene to give 1.98 g of bright red powder after being dried at 110 °C under vacuum. The solid did not melt or decompose below 320 °C and was insoluble in hot DMF, THF, and concentrated HCl. Anal. Calcd for $C_8N_4S_4O_2$:

Table II. Yield and Properties of Dicarboxamides[a]

amine	method	yield, %	mp,[b] °C	color	formula
NH_3	C	85	>350 (Me_2SO)	yellow	$C_8H_4N_2S_4O_2$
CH_3NH_2	B	85	353-355 (DMF)	pale yellow	$C_{10}H_8N_4S_4O_2$
$(CH_3)_2NH$	B	47	220-223 (DCE)	pale yellow	$C_{12}H_{12}N_4S_4O_2$
$C_6H_5NHNH_2$	A	83	325 dec (pyr-EtOH)	yellow	$C_{20}H_{14}N_6S_4O_2 \cdot H_2O$
p-$CH_3C_6H_4NH_2$	A	98	353-356 (DMF)	pale yellow	$C_{22}H_{16}N_4S_4O_2$
p-$CH_3OC_6H_4NH_2$	A	98	336-339 (DMF)	yellow	$C_{22}H_{16}N_4S_4O_4$
p-$NO_2C_6H_4NH_2$	A	99	385-387 (DMF)	deep yellow	$C_{20}H_{10}N_6S_4O_6$
o-$NO_2C_6H_4NH_2$	A	82	350-353 (DMF)	deep yellow	$C_{20}H_{10}N_6S_4O_6$
p-$NO_2C_6H_4NHCH_3$	A	96	356-358 (DMAC)	deep yellow	$C_{22}H_{14}N_6S_4O_6$
o-$NO_2C_6H_4NHCH_3$	A	92	313-316 (Me_2SO)	deep yellow	

[a] Satisfactory elemental analyses for C, H, N, and S were found for all compounds. [b] Recrystallization solvent in parentheses.

Table III. ^{13}C NMR Chemical Shifts and Probable Assignments



compd	solv	chemical shift, δ			
		C_5	C_4	C_3	others
4	Me_2SO-d_6	133.0	127.2	153.2	108.3 (CN)
18	Me_2SO-d_6	143.97 (d)	123.57	155.41	
21	$AsCl_3$	150.93	130.85	156.06	185.37 (CO), 122.22, 129.94, 135.27 (p), 137.09
26[a]	Me_2SO-d_6	148.72 (d), 146.44 (d)	124.93, 118.76	153.85, 160.68	40.82 (CH_3 in CD_3CN)
27	$CDCl_3$	143.69, 126.99	123.7, 123.2	156.82, 156.04	39.71 (CH_3), 113.93 (CN)
29[a]	Me_2SO-d_6	156.78, 157.95	136.89, 135.46	163.02, 165.49	

[a] Exo and endo isomers.

C, 30.8; N, 17.9; S, 41.1. Found: C, 30.7; N, 17.5; S, 40.6.

(b) Acetamide 24. A bright yellow suspension of 11.63 g of **20** in 600 mL of acetic anhydride was heated at 106 °C for 4.5 h. The resulting thick orange suspension was cooled, filtered, and washed with 95% ethanol to give 10.09 g (92%) of **24** as orange solid. Recrystallization from 550 mL of pyridine (yellow solution) afforded 9.30 g (84.7%) of an analytical sample, mp 270 °C dec. Anal. Calcd for $C_{10}H_8N_4S_4O_2$: C, 34.9; H, 2.3; N, 16.3. Found: C, 34.8; H, 2.6; N, 16.0.

(c) Benzylurethane 25. A mixture of 6.73 g of **20** and 300 mL of benzyl alcohol was refluxed for 30 min, cooled, filtered, and washed with ether to give 8.40 g (87%) of **25** as colorless solid. Recrystallization from Me_2SO afforded an analytical sample, mp 294–295 °C. Anal. Calcd for $C_{22}H_{16}N_4S_4O_8$: C, 50.0; H, 3.1; N, 10.6; S. 24.3. Found: C, 49.9; H, 3.2; N, 10.6; S, 24.3.

1,4-Dithiino[3,4-*c*;6,5-*c'*]diisothiazole-3,7-diamine (22). (a) From 20. A mixture of **20** (21.9 g, 0.06 mol), *tert*-butyl alcohol (30 mL), and *p*-xylene (500 mL) was refluxed overnight while the pot temperature rose from 90 to 100 °C. The *tert*-butyl alcohol was distilled until the pot temperature rose to 138 °C, and the mixture was refluxed 1 h longer. The mixture was cooled, filtered, and washed with toluene and ether to give **22** (13.5 g, 87%) as a tan solid. The IR spectrum was essentially identical with that of an analytical sample described below.

(b) From 24. A mixture of 4.48 g of **24** and 100 mL of concentrated HCl was refluxed for 4 h, cooled, diluted with 50 mL of water, and filtered to give 2.85 g of brown solid, which was dissolved in 175 mL of hot pyridine and treated with charcoal. The filtered solution was diluted with 95% ethanol to give 2.07 g (61%) of **22** as tan solid. An analytical sample was obtained by recrystallizations from aqueous hydrochloric acid and from a DMF–ethanol mixture, with considerable loss, as colorless crystals: mp 230 °C dec; IR (KBr) 2.86, 3.01, 3.13, 6.10, 6.49, 7.04, 7.69, 7.87, 8.92, 10.31, 12.90, 14.49 μm. Anal. Calcd for $C_6H_4N_4S_4$: C, 27.7; H, 1.6; N, 21.5. Found: C, 27.9; H, 1.8; N, 21.3. Acetylation of **22** with acetic anhydride quantitatively afforded **24**.

(c) From 25. A mixture of 7.6 g of **25** and 250 mL of 30% HBr in acetic acid was refluxed for 10 h while HBr gas was continuously passed through. The dark mixture was cooled, filtered, and washed with acetic acid and ether to give 6.44 g of crude **22** as brown solid, which was difficult to purify.

Esters of 17. The following esters were prepared from the acid chloride **41** and an alcohol.

(a) Dimethyl ester: mp 240–243 °C (n-C_4H_9Cl); UV (CH_2Cl_2) λ_{max} 272 nm (ε 12100), 280 (6100). Anal. Calcd for $C_{10}H_6N_2S_4O_4$: C, 34.7; H. 1.8; N, 8.1. Found: C, 35.0; H, 1.9; N, 8.0.

(b) Diethyl ester: mp 191–193 °C (n-C_4H_9Cl). Anal. Calcd for $C_{12}H_{10}N_2S_4O_4$: C, 38.5; H, 2.7; N, 7.5; S, 34.3. Found: C, 38.8; H, 2.9; N, 7.7; S, 34.3.

(c) Dibenzyl ester: mp 245–246 °C (Me_2SO). Anal. Calcd for $C_{22}H_{14}N_2S_4O_4$: C, 53.0; H, 2.8; N, 5.6. Found: C, 53.0; H, 3.1; N, 5.6.

(d) Diphenyl ester: mp 220 °C dec ($C_6H_5CH_3$); UV (CH_3CN) λ_{max} 375 nm (ε 12000), 283 (9700), 220 (35000). Anal. Calcd for $C_{20}H_{10}N_2S_4O_4$: C, 51.1; H, 2.1; N, 6.0; S, 27.3. Found: C, 50.6; H, 2.4; N, 6.4; S, 27.6.

Amides of 17. The amides in Table II were prepared by method A, treatment of the acid chloride **41** with 4–6 equiv of amine in boiling dichloroethane for 0.5–2 h, or by method B, treatment of **41** with an aqueous solution of amine at ambient temperature. The parent dicarboxamide was prepared from the nitrile **4** by use of basic hydrogen peroxide (method C).

3,7-Dibenzoyl-1,4-dithiino[2,3-*c*;6,5-*c'*]diisothiazole 21. A suspension of **41** (3.55 g) in 100 mL of benzene was treated with 7.0 g of aluminum chloride at 5 °C. The orange mixture was refluxed for 5 h, cooled, and poured into a mixture of ice and dilute HCl. The solid (4.31 g) was filtered and recrystallized from 800 mL of dichloroethane to give 2.83 g (63.5%) of **21** as deep yellow solid, mp 290–291 °C. Another recrystallization from DMF afforded an analytical sample: mp 291–292 °C; UV (CH_3CN, not all soluble) λ_{max} 405 nm (ε >6800), 303 (>10000), 266 (>11000), 234 (>14000). Anal. Calcd for $C_{20}H_{10}N_2S_4O_2$: C, 54.8; H, 2.3; N, 6.4; S, 29.3. Found: C, 54.7; H, 2.5; N, 6.4; S, 29.3.

4-Methyl-1,4-dithiinium[2,3-*c*;6,5-*c'*]diisothiazole Tetrafluoroborate (26). A mixture of **18** (4.6 g, 0.02 mol) and trimethyloxonium tetrafluoroborate (3.0 g, 0.02 mol) in CH_2Cl_2 (200 mL) was heated under an atmosphere of nitrogen at 40 °C for 5 h and then cooled. Crude **26** (4.85 g, 73%) was separated by filtration. Recrystallization from ethyl acetate/acetonitrile (1:1) gave pale yellow needles of **26**: mp 220 °C (dec); UV (CH_3CN)

λ_{max} 358 nm (ε 5080), 282 (8800); ^{1}H NMR (CD_3CN) δ 4.00 (s, 3 H), 8.90 (s, 1 H), 8.93 (s, 1 H); ^{13}C NMR (Me_2SO-d_6, Cr(acac)) δ 148.72 (CH), 146.44 (CH), 118.76, 124.93, 153.85, 160.68; ^{13}C NMR [CD_3CN, Cr(acac)] δ 40.82 (CH_3), 148.44 (CH), 144.34 (CH).

8-Methyl-1,4-dithiino[3,4-*b*;3′,4′-*e*]diisothiazole-1-carbonitrile (27). A solution of tetraethylammonium cyanide (1.7 g, 0.01 mol) in acetonitrile (50 mL) was added over a 15-min period to a solution of **26** (3.3 g, 0.01 mol) in acetonitrile (100 mL) at 15 °C, and crude **27** (2.21 g, 98%) was isolated by filtration. Compound **27** was washed with acetonitrile and ether. Recrystallization from *n*-butyl chloride (or acetone) gave analytically pure **28**: mp 140–142 °C; IR (Nujol) 4.55, 6.21, 6.49 μm; ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 3 H), 7.05 (s, 1 H), 8.47 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 39.71 (CH_3), 113.93 (CN), 123.20, 123.70, 126.99 (CH), 143.69 (CH), 156.04, 156.82. Anal. Calcd for $C_8H_5N_3S_4$: C, 35.4; H, 1.9; N, 15.5; S, 47.3. Found: C, 35.5; H, 2.2; N, 15.2; S, 47.2.

1,4-Dithiino[3,4-*c*;6,5-*c*]diisothiazole 4-Oxide (30).[38] A solution of trimethylsilyl nitrate[39] (2.8 g, 0.02 mol) in CH_2Cl_2 (20 mL) was added dropwise to a suspension of **18** (2.3 g, 0.01 mol) in CH_2Cl_2 (70 mL). The mixture was stirred at room temperature for 3 days and filtered. Recrystallization from ethanol gave 1.4 g (29%) of **24**: mp 183–185 °C; NMR (Me_2SO-d_6) δ 9.4 (s, 1 H), 10.22 (s, 1 H); mass spectrum, *m/e* 245.9070 (calcd *m/e* 245.9050). Anal. Calcd for $C_6H_2N_2S_4O$: C, 29.3; H, 0.8; N, 11.4. Found: C, 30.1; H, 1.2; N, 11.6.

1,4-Dithiino[3,4-*b*;3′,4′-*e*]diisothiazole 4,8-Dioxide (29).[40] A KelF vessel was charged with **18** (2.3 g, 0.01 mol), evacuated, and cooled in liquid N_2. HF (40 mL) was distilled directly in. The vessel was allowed to warm. When the HF had entirely melted, sodium nitrate (2.55 g, 0.03 mol) was added in one portion. The vessel was sealed and allowed to warm to room temperature. After the mixture was stirred for 7 h, the HF was allowed to evaporate under a gentle stream of nitrogen and then under aspirator vacuum to remove traces of HF. The remaining yellow solid was washed well with water, dried under vacuum, and recrystallized from Me_2SO, giving 2.68 g of product: mp >240 °C; IR (Nujol) 3.25, 6.91, 9.52 μm; ^{1}H NMR (Me_2SO-d_6) δ 10 (two peaks of equal intensity); mass spectrum, *m/e* 262. Anal. Calcd for $C_6H_2S_4N_2O_2$: C, 27.5; H, 0.8; S, 48.9; N, 10.7; mol wt 262. Found: C, 27.5; H, 1.1; N, 10.8; S, 48.7.

1,4-Dithiino[3,4-*b*;3′,4′-*e*]diisothiazole 4,4,8-Trioxide (31). A solution of **17** (5.0 g, 0.016 mol) in 5% NaOCl (200 mL) was heated at 65–67 °C for 3 h. The mixture was cooled and filtered, and the solid **31** was washed with H_2O, 95% EtOH, and ether to give 2.08 g (47%) colorless **31**. Recrystallization from a DMF–95% EtOH mixture gave analytically pure **31**: mp 235 °C dec; IR (KBr) 7.46, 8.62, 8.93, 9.09 μm; mass spectrum, *m/e* 277.8930 (calcd *m/e* 277.8948); the sample also showed traces of *m/e* 293.8848 (calcd *m/e* 293.8897), indicating the presence of trace amounts of the disulfone. Anal. Calcd for $C_6H_2N_2S_4O_3$: C, 25.9; H, 0.7; N, 10.1; S, 46.1. Found: C, 26.1; H, 1.0; N, 9.8; S, 45.7.

Registry No. **1**, 2448-55-7; **4**, 63419-80-7; **4** radical ion, 75083-00-0; **6**, 5466-54-6; **7**, 66232-78-8; **9**, 75083-01-1; **12**, 75083-02-2; **15**, 66393-25-7; **16**, 66232-81-3; **17**, 63419-82-9; **17** K salt, 66232-83-5; **17** NBu_4 salt, 63459-58-5; **17** amide, 75083-03-3; **17** methylamide, 75083-04-4; **17** dimethylamide, 63419-84-1; **17** phenylhydrazide, 75083-05-5; **17** *p*-methylphenylamide, 63419-90-9; **17** *p*-methoxyphenylamide, 63419-88-5; **17** *p*-nitrophenylamide, 63419-89-6; **17** *o*-nitrophenylamide, 63419-91-0; **17** methyl-*p*-nitrophenylamide, 63419-92-1; **17** methyl-*o*-nitrophenylamide, 63419-93-2; **17** dimethyl ester, 63419-85-2; **17** diethyl ester, 63419-86-3; **17** dibenzyl ester, 63419-87-4; **17** diphenyl ester, 75083-06-6; **18**, 63419-81-8; **18**·2HBr, 75083-07-7; **20**, 75082-98-3; **20** polymer, 75082-99-4; **21**, 75083-08-8; **22**, 75083-09-9; **24**, 75083-10-2; **25**, 75083-11-3; **26**, 75083-13-5; **27**, 75083-14-6; **29**, 75083-15-7; **30**, 75101-69-8; **31**, 75083-16-8; **41**, 63419-83-0; sulfur, 7704-34-9; 2-oxo-4,5-dicyano-1,3-dithiacyclopentene, 934-31-6; 3,4-bis(methylthio)isothiazole-5-carbonitrile, 75083-17-9; 3,4-dimercaptotoluene, 496-74-2; dichloromaleonitrile, 6613-48-5; dichloroquinoxaline, 2213-63-0.

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Reactions of Trimethylsilyl Azide with Heterocumulenes

Otohiko Tsuge,* Satoshi Urano, and Koji Oe

Research Institute of Industrial Science, Kyushu University 86, Hakozaki, Higashi-ku, Fukuoka 812, Japan

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Trimethylsilyl azide (TMSA) reacted with aryl isocyanates to give arylcarbamoyl azides, 1-aryl-5(4*H*)-tetrazolinones, and/or 1-aryl-4-(arylcarbamoyl)-5(4*H*)-tetrazolinones, whose yields were dependent on the reaction conditions. The reaction between TMSA and benzoyl or thiobenzoyl isocyanates provides a facile method for the preparation of 5-aryl-3-hydroxy-1,2,4-oxadiazoles or -1,2,4-thiadiazoles, respectively. However, with phenyl or benzoyl isothiocyanate, 1-anilino-1,2,3,4-thiatriazole or benzoylcyanamide was obtained in low yield, respectively. TMSA reacted with carbodiimides to afford the corresponding 5-aminotetrazoles. Tetraphenylsuccinimide, *N*-(diphenylacetyl)tetraphenylsuccinimide, 1,3-bis(diphenylmethyl)urea, and/or benziloylamide were obtained from the reaction of TMSA with diphenyl ketene. The pathways for the formation of the above products are also described.

It is known that trimethylsilyl azide (TMSA) is a good reagent in organic syntheses. In analogy with organic azides, TMSA behaves as a 1,3-dipole toward acetylenes,[1] olefins,[2] and nitriles[2a,3] to give the corresponding cycloadducts. The reaction of TMSA with carboxylic acid chlorides,[4] anhydrides,[5] esters,[6] and lactones[6] provides a facile synthetic route to a variety of isocyanates which in some cases directly cyclized to heterocyclic compounds. It has also been reported that TMSA reacted with aliphatic aldehydes and epoxides to form the corresponding tri-

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