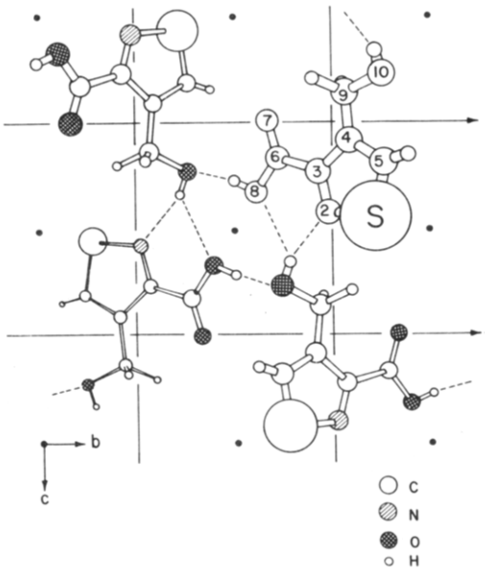

Figure 1. Crystal structure of **12**.

space group $P2_1/n$ with Z = 4; 562 "observed" intensities measured on an automatic diffractometer (Cu Kα; λ 1.542 Å) were used for the solution and least-squares refinement of structure. Patterson and Fourier analyses revealed an atomic arrangement consistent with the 3,4-disubstituted isothiazole **12**. Refinements of the coordinates and anisotropic temperature factors, including the coordinates (but not temperature factors) of all five hydrogen atoms evident in a difference map, converged to $R = 0.06$.[21]

The heterocyclic ring is planar to within 0.004 Å and the S–N and S–C bond lengths are 1.655 (2) and 1.704 (2) Å, respectively. The carbonyl oxygen O(7) is syn to C(4) [torsional angle O(7)–C(6)–C(3)–C(4) = 1°]. There is no intramolecular hydrogen bonding; instead, O(10) adopts an anti conformation with respect to C(3) and the carboxyl group [torsional angle O(10)–C(9)–C(4)–C(3) = 179°] and is *inter*molecularly hydrogen bonded to a glide related molecule [O(8) ··· O(10) distance = 3.01 Å; O(10) ··· N(2) distance = 2.94 Å].

In addition, the carboxyl hydrogen is hydrogen bonded to O(10) of a screw-related molecule [O(8) ··· O(10) distance = 2.66 Å]. A drawing of this hydrogen-bonded network is shown in Figure 1.

Acknowledgments. We wish to thank Dr. M. S. Puar for the 100-MHz NMR data and for helpful discussion during this investigation. We are also indebted to Dr. P. T. Funke for the mass spectral data and Mr. H. Basch for microbiological data.

Registry No.—**1a,** 24647-47-0; **2a,** 28180-80-5; **2b,** 33465-36-0; **6a,** 64024-46-0; **6b,** 64024-47-1; **8c,** 58800-55-8; **10,** 3595-22-0; **11,** 64024-48-2; **12,** 64024-49-3; methanethiol, 74-93-1.

Supplementary Material Available: Tables of fractional coordinates, temperature factors, and interatomic angles and distances (3 pages). Ordering information is given on any current masthead page.

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p-Quinobis(1,3-benzodithiole) *S*-Oxide. An Unusual Vinylogous Tetrathiafulvalene Derivative

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The purple-black title compound **9** has been synthesized from *o*-benzenedithiol in several steps, the last of which involves a novel base-catalyzed vinylogous Pummerer dehydration of a sulfoxide. Some chemical and physical properties of **9,** which may be viewed as a push–pull stabilized *p*-quinodimethane, are described.

The discovery of the high solid-state electrical conductivity of the charge-transfer complex of tetrathiafulvalene (TTF, **1**) and tetracyanoquinodimethane (TCNQ, **2**)[1] has provided the impetus for the synthesis of a variety of structural modifications of both of the above-mentioned molecules.[2]

The unknown heterocycles **3** and **4** present particularly interesting structural features, since they combine in one molecule the substituted *p*-quinodimethane system of TCNQ with the two 1,3-dithiolidine moieties of TTF. This paper describes the synthesis and some chemistry of the monosul-

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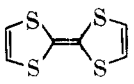
foxide of **4**, namely, *p*-quinobis(1,3-benzodithiole) *S*-oxide (**9**).



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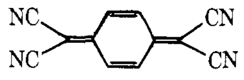

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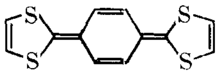

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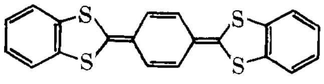

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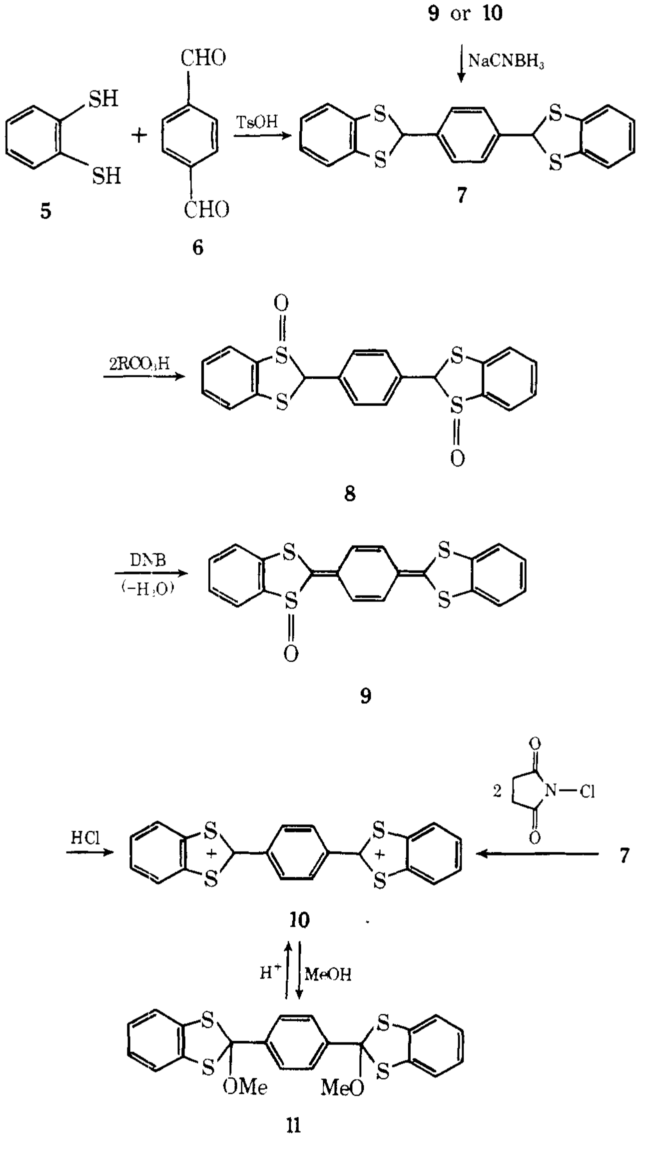
Results

Synthesis of the Quinonoid Sulfoxide 9. *o*-Benzenedithiol (**5**)[3] was reacted with terephthalaldehyde (**6**) in the presence of *p*-toluenesulfonic acid to give (73%) the bisthioketal **7**, mp 175 °C (dec). Attempts to effect a direct dehydrogenation of **7** to the quinodimethane **4** using chloranil or dichlorodicyanobenzoquinone (DDQ) lead to the disappearance of **7**, although no characterizable reaction product could be isolated. Oxidation of thioketal **7** by *m*-chloroperbenzoic acid proceeded cleanly only in the cold in the presence of the mild acid scavenger disodium hydrogen phosphate. When only 1 equiv of peracid was used, 33% of starting material could be recovered, showing the oxidized material to be a mixture of mono- and disulfoxides; these could not be separated due to their great lability on a variety of adsorbents. When a little over 2 equiv of peracid was used, NMR analysis showed the disappearance of the thioketal singlet at δ 6.12, and its replacement by a more shielded singlet at δ 5.8, attributable to the resulting stereoisomeric disulfoxides **8**. Direct warming of the latter with diazabicyclononene (DBN) and pyridine in dichloromethane led to the rapid appearance of an intense permanganate purple color and the separation, in good yield (37%), of the quinodimethane **9**.



Properties and Reactions of the Quinonoid Sulfoxide 9. Sulfoxide **9** is a purple-black, microcrystalline powder; on grinding in a mortar it acquires a striking bronze-like metallic sheen. It has no definite melting point, but turns red around 180 °C and slowly decomposes above 270 °C. It is totally insoluble in nonpolar solvents such as benzene or hexane; it is only very slightly soluble in such polar solvents as pyridine, dimethylformamide and hexamethylphosphoramide, in which it gives purple solutions due to an absorption maximum at about 530 nm. Attempted soxhlet recrystallization from the latter solvents leads to slow decomposition; however, solvent leaching of all impurities from **9** is readily carried out, the insoluble purple-black residue being directly of analytical purity.

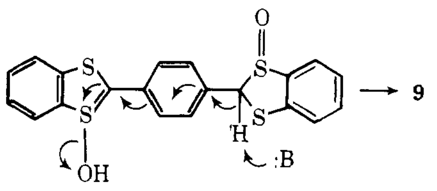
The purple sulfoxide **9** is rapidly destroyed by concentrated hydrochloric acid. The resulting yellow bisdithiolium ion **10** is formed cleanly, and may be isolated in good yield (66%) as its crystalline bisfluoborate salt. An independent synthesis of **10** was achieved by the *N*-chlorosuccinimide oxidation of thioketal **7** in hot acetonitrile.

Sulfoxide **9** was decolorized readily by sodium cyanoborohydride at pH 4 to give the starting thioketal **7**. The dication **10** was also found to be reduced to **7** by the reagent.

Finally, sulfoxide **9** was found to react with methanol in the presence of a small amount of *p*-toluenesulfonic acid to give the white crystalline dimethoxy compound **11**. The latter was quite stable under basic conditions, but was converted by strong acid to the yellow dication **10**. Again, the latter cation was the probable reaction intermediate; as expected, it reacted slowly with methanol to give the methoxy compound **11**.

Discussion

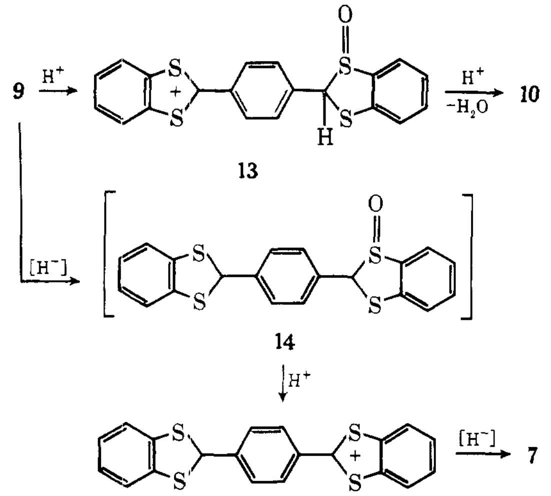
The reactions reported above include several examples of very facile Pummerer-type sulfoxide dehydrations. Thus, the dehydration of the disulfoxide **8** to the purple sulfoxide **9** is the first reported example of a *base-catalyzed vinylogous* sulfoxide dehydration.[4] It presumably involves dehydration of the "thiaenol" **12** of **8** as shown below:



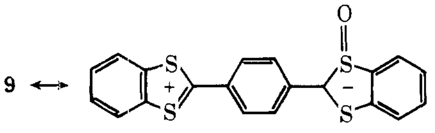
12

The conversion of **9** to dication **10** by aqueous acid must involve protonation of **9** to the cation sulfoxide **13**, followed by an unusually rapid acid-catalyzed Pummerer dehydration of **13** to **10**. A similar rapid dehydration of a 1,3-dithiole monosulfoxide **14** is probably involved in the cyanoborohydride reduction of sulfoxide **9** to thioketal **7**.

The unusual insolubility of sulfoxide **9** attests to the existence of strong forces in the crystal lattice which bind the individual molecules together. These forces are undoubtedly electrostatic in nature and result from the fact that the polar



canonical form **15** is undoubtedly a very important contributor to the structure of **9**. Sulfoxide **9** is therefore to be viewed as a new type of push-pull stabilized *p*-quinodimethane, other types of which have been previously prepared by Gompper and co-workers.[5]



15

Studies aimed at the conversion of sulfoxide **9** and dictation **10** into the parent *p*-quinodimethane **4** are presently under investigation in our laboratory.

Experimental Section

Melting points are uncorrected. NMR ($CDCl_3$ containing tetramethylsilane as internal standard) and ultraviolet and mass spectra were determined using Varian A-60 and Perkin-Elmer 202 and 270B spectrometers, respectively.

1,4-Phenylenebis(benzodithioketal) (7). A mixture of terephthalaldehyde (6.3 g; 0.5 equiv) and *o*-benzenedithiol[3] (14 g; 1 equiv) in 300 mL of benzene containing a trace (~50 mg) of *p*-toluenesulfonic acid was refluxed using a Dean–Stark trap, until no more water separated. The solid, mp 173–175 °C (dec), which crystallized upon cooling (14.3 g; 73%) was filtered. Concentration of the filtrate yielded a second crop (2.4 g) of less pure material. An analytical sample, mp 175 °C (dec), was obtained by recrystallization from absolute ethanol containing benzene: mass spectrum M^+ 382; NMR δ 6.12. Anal. Calcd for $C_{20}H_{14}S_4$: C, 62.83; H, 3.69. Found: C, 62.69; H, 3.78.

***p*-Quinobis(1,3-benzodithiole) *S*-Oxide (9).** A mixture of solutions of bisthioketal (3.82 g; 1 equiv) in 200 mL of methylene chloride and 100 mL of aqueous 5% Na_2HPO_4 was cooled to 10 °C. A cold solution of *m*-chloroperbenzoic acid (3.44 g; 2 equiv) in 200 mL of methylene chloride was added within 15 min, with good stirring. The organic layer was separated, washed once with aqueous Na_2HPO_4 solution, and filtered through phase-transfer filter paper into a flask containing a solution of 2 mL of DBN in 10 mL of CH_2Cl_2. The dark-violet solution was concentrated to half the volume, treated with 50 mL of pyridine, and warmed for 10 min on the steam bath. The black solid was filtered, washed with pyridine and methylene chloride, and dried to yield sulfoxide **9**, mp >270 °C (dec) (1.4 g; 37%). An analytical sample was obtained by boiling **9** quickly with pyridine and filtering: mp >270 °C (dec); visible spectrum λ_{max} pyridine 410 (sh), 478, 530 nm; mass spectrum *m/e* 380 (M − 16). Anal. Calcd for $C_{20}H_{12}OS_4$: C, 60.55; H, 3.05; S, 32.36. Found: C, 60.35; H, 3.07; S, 32.08.

***p*-Phenylenebis(1,3-benzodithiolium) Fluoborate (10).** (a) Finely ground **9** (1 g) was heated with a mixture of glacial acetic acid (200 mL), acetic anhydride (20 mL), and commercial fluoboric acid solution (50 mL). The yellow mixture was filtered hot, concentrated, and treated with anhydrous ether to give a yellow precipitate of crude **10** (0.93 g; 66%), decomposition above 250 °C. Recrystallization from acetonitrile containing fluoboric acid yielded pure yellow needles (0.8 g), decomposition above 280 °C. Anal. Calcd for $C_{20}H_{12}S_4B_2F_8$: C, 43.33; H, 2.18; S, 23.15. Found: C, 43.59; H, 2.12; S, 22.96.

(b) A suspension of bisketal **7** (0.191 g) and *N*-chlorosuccinimide (0.266 g) in 30 mL of acetonitrile was heated gently. Within 0.5 h the color turned green, cleared, and precipitated as an orange-brown solid. The mixture was cooled and filtered, and the precipitate was washed with acetonitrile–ether. The insoluble precipitate (0.236 g) was heated with 25 mL of fluoboric acid (50% solution) and filtered hot. The yellow crystals were filtered and washed with cold dilute fluoboric acid followed by ether to yield the fluoborate of bis(**10**) (0.136 g; 50%), mp decomposition above 280 °C, identical to the sample obtained in a (mp, IR spectrum).

Addition of Methanol to 9 (11). An intimate mixture of **9** (0.300 g) and a trace of *p*-toluenesulfonic acid in 1 mL of methanol was stirred for 2 h at room temperature. A chloroform solution of crude product (0.33 g) was filtered through basic alumina to yield **11** (0.28 g), mp 205–210 °C. Recrystallization from methanol–benzene yielded very pure **11**: mp 210–211 °C (turns pink); mass spectrum M^+ 442, *m/e* 411, 380, 335, 303, 259, 229, 228, 227, 190; NMR 8.0 (m, 12 ArH), 3.5 (s, 6 H, 2 OMe). Anal. Calcd for $C_{22}H_{18}O_2S_4$: C, 59.73; H, 4.10; S, 28.92. Found: C, 59.83; H, 4.10; S, 28.52. Compound **11** could also be made by triturating **9** with methanolic hydrogen chloride in the cold.

$NaCNBH_3$ Reduction of 9. To a mixture (10 mL) of dilute hydrochloric acid (10%) in glacial acetic acid (2 mL) was added well-powdered **9** (100 mg), followed by excess $NaCNBH_3$ (100 mg). Dilution followed by extraction with CH_2Cl_2 afforded the bisthioketal **7** (35 mg), mp 170 °C, identical in all respects (mixture mp, IR) to authentic **7**.

$NaCNBH_3$ Reduction of Bisthiolium Fluoborate of 10. To a suspension of **10** fluoborate (136 mg) in glacial acetic acid (5 mL) containing 50% HBF_4 (1 mL) and CH_2Cl_2 (~5 mL), excess $NaCNBH_3$ (100 mg) was added with swirling. Reduction was instantaneous. Dilution with water followed by separation of the organic layer and the usual workup yielded 70 mg (77.8%) of **7**, mp 170 °C, after recrystallization, identical in all respects to authentic **7**.

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Registry No.—**5**, 17534-15-5; **6**, 623-27-8; **7**, 63866-46-6; **9**, 63866-45-5; **10**, 63866-44-4; **11**, 63866-42-2.

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