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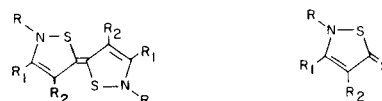
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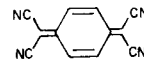
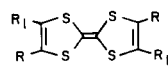
A series of 5,5'-biisothiazolylidenes has been prepared from isothiazolidine-5-thiones and their ability to form charge-transfer complexes with electron acceptors has been investigated.

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Only a few examples of 5,5'-biisothiazolylidenes have been described (1). These were *trans*-benzo-derivatives, (**1f**), prepared by thermal extrusion of sulfur from benzoisothiazoline-5-thiones (**2f**). These compounds are iso-electronic with 3,3'-bis-1,3-dithiolylidenes, better known as tetrathiafulvalenes (**3**), which have been the subject of intensive work since the discovery of their charge-transferring ability with suitable  $\pi$  electron acceptors, *eg.* tetracyanoquinodimethane (**4**) (TCNQ) (2). The resulting 1:1 complexes exhibit interesting electrical properties. In this note we describe the preparation of some monocyclic biisothiazolylidenes (**1a-e**) and investigation of their ability to form charge transfer complexes. The preparation was approached *via* the coupling of isothiazoline-5-thiones (**2**). While methods for the synthesis of monocyclic isothiazoline-5-thiones are scarce, 4-phenyl derivatives (**2a-e**) are readily available by treatment of 4-phenyl-1,2-dithiole-3-thiones with bromine, followed by primary amines (3). Coupling was effected with concomitant desulfurization, by treatment with triethyl phosphite in benzene. Trivalent phosphorus compounds have been used for 1,3-dithiole-2-thiones with success, although usually these contain electron withdrawing substituents (4). Reaction times were sometimes critical (See Table) as polymeric products formed readily. Attempts at thermal coupling failed, despite the ready coupling of benzoisothiazoline-5-thiones (2), and octacarbonyl dicobalt, which has been used recently in the coupling of 1,3-dithiole-2-thiones to form tetrathiafulvalenes (5) and of other thiones to give ethylene

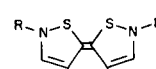
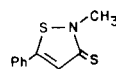


- 1a**, R = CH<sub>3</sub>, R<sub>1</sub> = H, R<sub>2</sub> = Ph  
**1b**, R = *t*Bu, R<sub>1</sub> = H, R<sub>2</sub> = Ph  
**1c**, R = C<sub>6</sub>H<sub>11</sub>, R<sub>1</sub> = H, R<sub>2</sub> = Ph  
**1d**, R = Ph, R<sub>1</sub> = H, R<sub>2</sub> = Ph  
**1e**, R = C<sub>6</sub>H<sub>4</sub>pCH, R<sub>1</sub> = H, R<sub>2</sub> = Ph  
**1f**, R = alkyl, aryl; R<sub>1</sub> = R<sub>2</sub> = -(CH=CH)<sub>2</sub>-



**3**

**4**



- 5a**, R = H  
**5b**, R = Ph

derivatives (**6**), gave only polymer in this case. Interestingly, two isothiazoline-3-thione derivatives (**5a**) and (**5b**) failed to couple by this method. While these biisothiazolylidenes could exist in *cis* or *trans* forms, examination of a space filling model indicated that the *cis* isomer (**6**) would exhibit great steric strain. In fact careful analysis of the reaction products indicated that only one isomer, likely the *trans* isomer, was formed in each case.

Attempts were made to form charge transfer complexes of these materials with TCNQ and with iodine. In each

Table 1

Preparation of 5,5'-Biisothiazolidines **1a-e** from Isothiazoline-5-thiones

Compound	R	Time(h)	Yield(%)	m.p. °	C	Analysis (%)						
						Calcd.			Found			
						H	N	S	C	H	N	S
<b>1a</b>	Me	0.5	38	201-203	68.55	5.15	8.0	18.30	68.90	4.85	7.65	17.85
<b>1b</b>	C(Me) <sub>3</sub>	0.25	54	167-169	71.90	6.90	6.45	14.75	71.50	6.95	6.65	14.55
<b>1c</b>	C <sub>6</sub> H <sub>11</sub>	1.0	42	95-98	74.05	7.00	5.75	13.15	73.85	7.10	5.65	12.85
<b>1d</b>	C <sub>6</sub> H <sub>5</sub> (a,b)	0.5	64	219-224	75.95	4.64	5.90	13.50	76.15	4.65	5.45	13.15
<b>1e</b>	C <sub>6</sub> H <sub>4</sub> p-Me (a)	2.0	62	211-212	76.50	5.20	5.60	12.75	16.20	5.25	5.65	12.90

(a) These reactions were performed under reflux. (b) These reaction products were purified by chromatography.

case these were unsuccessful. Evidently steric and/or electronic effects of the 4-phenyl substituent hinder the charge-transfer ability. On the other hand, the benzo-analog (**1f**), although it did not form a derivative with TCNQ, did give a complex with iodine, which crystallised from chloroform as deep violet cubes. While not exact, the analysis corresponded closely to a bisisothiazolium diiodide, I<sub>2</sub> formulation, *ie.* a 1:2 complex. It is known that monocyclic isothiazolium salts may be obtained as triiodides (6). Attempts to obtain a satisfactory analysis for an exactly 1:2 complex were unsuccessful, and on heating *in vacuo* the iodine decreased, most likely by dissociation of the complex. Investigation of this research using less substituted isothiazoles is continuing.

#### EXPERIMENTAL

##### Preparation of bisisothiazolylienes (**1a-e**).

The thiones (**2**) were dissolved in benzene with stirring at RT, and to the solutions were added the equivalent quantity of triethyl phosphite. After the appropriate times the solutions were evaporated *in vacuo* and the resulting oils either crystallised from ethanol, or were purified by chromatography on alumina in benzene. In some cases coupling was effected at reflux temperature. The results are summarized in the Table.

##### Attempted Reactions of bisisothiazolylienes with TCNQ.

Equimolar quantities of the bisisothiazolylienes with TCNQ were dissolved separately in the minimum volume of hot acetonitrile. The two solutions were mixed but on cooling TCNQ crystallised from solution. The bisisothiazolylidene was recovered from the mother liquors.

##### Reaction of 3,3'-dimethyl-5,5'-bibenzisothiazolylidene **1f** with Iodine.

A solution of iodine (0.70 g., 0.0026 mmole) in chloroform (50 ml.) was added to a solution of **1f** (0.4 g., 0.0013 mole) in chloroform (30 ml.) at 20° and after 24 hours deep violet cubes (0.8 g., 74%), m.p. 193-195°, were collected.

*Anal.* Calcd. for C<sub>16</sub>H<sub>4</sub>H<sub>2</sub>S<sub>2</sub>·2I<sub>2</sub>: C, 23.85; H, 1.75; N, 3.45; S, 7.95; I, 63.00. Found: C, 24.25; H, 1.75; S, 8.35; I, 62.05%.

Use of 1 molar equivalent of iodine also produces the same material. Prolonged drying *in vacuo* gave material with a lower iodine content.

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