

# Heterocyclic Sulfur Compounds. IC-Reaction of Ynamines with 1,2,4-Dithiazole Derivatives, and the Crystal Structure of *N*-(4-Diethylamino-5-methyl-1,3-dithiole-2-ylidene)-*p*-methoxythiobenzamide

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5-Aryl-1,2,4-dithiazole-3-ones and the corresponding thiones, reacting with ynamines, give a 1:1 adduct via a 2+3 cycloaddition. *N*-(1,3-Oxathiole-2-ylidene)thiobenzamides **4** and *N*-(1,3-dithiole-2-ylidene)thiobenzamides **5**, respectively, are obtained in this way.

The structures of compounds **4** and **5** have been established by mass spectrometry and <sup>1</sup>H NMR spectroscopy and confirmed by an X-ray structure analysis of *N*-(4-diethylamino-5-methyl-1,3-dithiole-2-ylidene)-*p*-methoxythiobenzamide (**5b**). The *N*-(1,3-dithiole-2-ylidene)thiobenzamide part of **5b** is almost planar, with bond lengths S(1)–C(2)=1.751(6), C(2)–S(3)=1.697(6), S(3)–C(4)=1.781(6), C(4)–C(5)=1.314(9), C(5)–S(1)=1.742(6), C(2)–N(6)=1.291(7), N(6)–C(7)=1.339(8), and C(7)–S(8)=1.664(6) Å. The S(1)⋯S(8) distance is 2.913(3) Å and the C(5)–S(1)⋯S(8) angle 159.7(3)°. The crystals of **5b** are monoclinic *P*2<sub>1</sub>/*c* with *a*=10.967(6), *b*=20.88(1), and *c*=7.941(6) Å, β=106.03(7)°, and *Z*=4.

While compounds **4** are rather unstable, compounds **5** are stable. The latter group of compounds is transformed into the corresponding benzamides by mercury(II) acetate treatment. One such compound has been prepared and its IR spectrum indicates a significant O–S interaction or partial bonding. The structure of this benzamide has been further confirmed by the <sup>1</sup>H NMR spectrum of its complex with tris(dipivaloylmethanato)europium.

Reaction of ynamines with 1,2-dithiole-3-ones or with the corresponding thiones or *N*-phenylimines opens the 1,2-dithiole ring either by a 2+3 cycloaddition or by a nucleophilic attack leading to a thiopyran derivative.<sup>1</sup> For reaction of ynamines with 1,3-dithiole-3-ones or 1,3-dithiole-3-thiones, on the other hand, a 2+2 cycloaddition preserving the dithiole ring has been observed.<sup>2</sup>

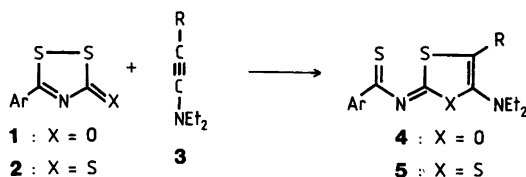
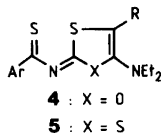


Table 1. Molecular compositions, yields (%), melting points (°C), and UV spectra for compounds 4 and 5. *N*-(1,3-Oxathiole-2-ylidene)thiobenzamides 4. *N*-(1,3-Dithiole-2-ylidene)thiobenzamides 5.



Ref.	X	Ar	R	Yield %	<i>F</i> <sup>c</sup>	Anal. <sup>a</sup>
4a	O	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	52	91 <sup>c</sup>	CHNOS
4b	O	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	48	92 <sup>c</sup>	CHNOS
4c	O	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	72	89 <sup>c</sup>	CHNOS
4d	O	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	93	114 <sup>c</sup>	CHNOS
5a	S	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	38	48 <sup>e</sup>	CHN
5b	S	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	32	94 <sup>c</sup>	CHNO
Ref.	UV Absorption spectra <sup>b</sup>					
4a	232(4.23)	325(4.14)			397(4.10)	
4b	232(4.19)	306(3.14) <sup>d</sup>	361(4.23)		396(4.03) <sup>d</sup>	
4c	225(4.45)	292(4.20)			416(3.94)	
4d	226(4.44)	308(4.06)	363(4.30)		396(4.10)	
5a	247(4.15)	260(4.18)	335(4.09)		437(4.37)	
5b	254(4.25)		376(4.23)		432(4.51)	

<sup>a</sup> Elementary analyses: deviations from theoretical values smaller than ±0.3%. <sup>b</sup> UV Spectra: λ nm(log ε). <sup>c</sup> Red crystals (ethanol). <sup>d</sup> Shoulder. <sup>e</sup> Black crystals (ethanol).

In this paper, we consider the reaction of 5-aryl-1,2,4-dithiazole-3-ones (1) and of the corresponding thiones (2) with ynamines (3). It is known that acetylenes can react with 5-aryl-1,2,4-dithiazole-3-thiones to give *N*-(1,3-dithiole-2-ylidene)thioamides<sup>3-7</sup> via a 2+3 cycloaddition. However, no reaction between an acetylene and a 1,2,4-dithiazole-3-one has been reported until now.

By reacting ynamines with 1,2,4-dithiazole-3-ones and the corresponding thiones, we have obtained *N*-(1,3-oxathiole-2-ylidene) thiobenzamides (4) and *N*-(1,3-dithiole-2-ylidene)-thiobenzamides (5), respectively, cf. Scheme 1.

*N*-(1,3-Oxathiole-2-ylidene)thiobenzamides (4). These compounds, 4a–4d, described in Table 1, have been obtained by reacting 5-aryl-1,2,4-dithiazole-3-ones with either 1-(diethylamino)propyne or 1-(diethylamino)-2-phenyl-acetylene. They form red crystals but are rather unstable at room temperature, and decompose after a few weeks into orange-yellow mixtures in which the initial dithiazolones have been identified. Furthermore, all attempts at replacing the thioamide sulfur by oxygen failed and resulted only in the regeneration of the initial dithiazolone.

Compounds 4 have been studied by <sup>1</sup>H NMR spectroscopy and mass spectrometry.

*NMR Spectroscopy.* <sup>1</sup>H NMR spectra for compounds 4, given in Table 2, show that in each reaction only one compound is obtained and not a mixture of *Z* and *E* isomers with respect to the juxtacyclic C–N bond.

One possible interpretation of the NMR spectra may therefore be a structure of type 4u, possibly with some elements of 4v (a 6-oxa-3,3aλ<sup>4</sup>-dithia-1-azapentalene), and another interpretation could be a highly polarized structure (4w) with rapid rotation around a

Table 2. <sup>1</sup>H NMR spectra for compounds 4 and 5.

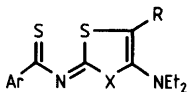
Ref.	Aromatic protons of Ar	CH <sub>3</sub> O	R	CH <sub>3</sub> (NEt <sub>2</sub> ) (6H, t, J 7 Hz)	CH <sub>2</sub> (NEt <sub>2</sub> ) (4H, q, J 7 Hz)
4a	7.16–7.56(3H, m); 8.23–8.56(2H, m)	—	2.13(3H, s)	1.06	3.03
4b	6.84 & 8.40 (qAB; J=9 Hz)	3.86(3H, s)	2.10(3H, s)	1.06	3.06
4c	7.20–7.76(3H, m) <sup>a</sup> ; 8.33–8.60(2H, m)	—	7.20–7.76(5H, m) <sup>a</sup>	1.10	3.16
4d	6.91 & 8.47 (qAB; J=9 Hz)	3.86(3H, s)	7.20–7.43(5H, m)	1.10	3.20
5a	7.16–7.56(3H, m); 8.23–8.53(2H, m)	—	2.30(3H, s)	1.03	2.91
5b	6.84 & 8.40 (qAB; J=9 Hz)	3.86(3H, s)	2.30(3H, s)	1.03	2.93

<sup>a</sup> Superimposed multiplets.

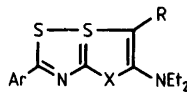
Table 3. Mass spectra for compounds 1, 2, 4 and 5. A: Molecular ion of dithiazolone 1 or of dithiazolethione 2, respectively, due to the fragmentation of the molecular ions of compounds 4 or 5, with formation of the molecular ion (B) of the ynamine. B: Molecular ion of the starting ynamine.

Ref.	M <sup>+</sup>	A <sup>+</sup>	B <sup>+</sup>	Ar-SCN <sup>+</sup>	Ar-CS <sup>+</sup>	Ar-CN <sup>+</sup>	S <sub>2</sub> <sup>+</sup>	R-CH <sup>+</sup>
4a	306(22)	195(23)	111(100)	—	121(32)	103(28)	64(84)	59(65)
4c	368 <sup>a</sup>	195(13)	173(40)	—	121(20)	103(39)	64(100)	121(20)
1a	195(27)	—	—	—	121(5)	103(30)	64(100)	—
4b <sup>b</sup>	336(6)	225(34)	111(77)	—	151(17)	133(100)	64(5)	59(16)
4d	398 <sup>a</sup>	225(38)	173(100)	—	151(6)	133(99)	64(4)	121(2)
1b	225(26)	—	—	—	151(5)	133(100)	64(5)	—
5a	322(12)	211(3)	111(100)	135(9)	121(27)	103(17)	64(44)	59(28)
2a	211(79)	—	—	135(100)	121(33)	103(55)	64(13)	—
5b <sup>b</sup>	352(42)	241(3)	111(100)	165(4)	151(48)	133(8)	64 <sup>a</sup>	59(21)
2b	241(89)	—	—	165(100)	151(38)	133(85)	64(15)	—

<sup>a</sup> Very weak signal. <sup>b</sup> Molecular formula of each fragment has been established by high resolving power (10<sup>4</sup>).



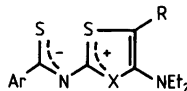
(u)



(v)

4 : X = O

5 : X = S



(w)

juxtacyclic C–N bond of low double bond character, *cf.* Scheme 2. The results from the X-ray structure study of *5b*, described later, indicate that the former interpretation is the correct one.

**Mass spectrometry.** The main fragments obtained from compounds *4* are given in Table 3. The molecular peak is very weak, particularly for compounds *4c* and *4d*, and the molecular ion is therefore rather unstable. In each case the main fragmentation leads to fragments corresponding to the two starting compounds, ynamine and dithiazolone. In the cases of *4a* and *4d* for instance, the most intense peak corresponds to the molecular ion of the ynamine. Furthermore, the metastable ion indicating the formation of the molecular ion of the ynamine from the molecular ion of compound *4*, has been observed in each case.

The  $S_2^{+}$  fragment which gives the most intense peak of the dithiazolone *1a* is very weak for *1b*, a difference which also appears in the fragmentation of the corresponding compounds *4a* and *4b*.

Other main peaks observed for compounds *4* also appear in the mass spectra of the starting dithiazolones and ynamines. One should note, however, that the amounts of  $Ar-CS^+$  fragments are greater from compounds *4* than from the corresponding dithiazolones.

The positions of the R and  $NEt_2$  groups on the 1,3-oxathiole ring are confirmed by the fact that the fragment  $R-CS^+$  is observed while the fragment  $R-CO^+$  is not.

These results, which show that compounds *4* are N-(1,3-oxathiole-2-ylidene)thiobenzamides, agree with a 2+3 cycloaddition mechanism and preclude a 2+2 mechanism such as the one observed with 1,3-dithiole-3-ones and 1,3-dithiole-3-thiones.<sup>2</sup>

The preceding results are in agreement with a theoretical study of the stability of compounds obtained by 2+3 cycloaddition between acetylenes and dithiazoles *1* or *2* or analogous compounds.<sup>8</sup> According to that study, the stability of the cycloaddition product depends upon the nature of the atom X and diminishes in the order S,  $CH_2$ , NR, O. This has been used to explain why no cycloaddition had been observed between an acetylene and a 1,2,4-dithiazole-3-one. The synthesis of compounds *4* is the first reaction of this type to be observed and this is probably due to the fact that the ynamine triple bond is more polarized than the triple bond of the acetylenes previously considered. Probably for the same reason, ynamines are the only acetylenes giving a 2+3 cycloaddition with 1,2-dithiole-3-ones.<sup>1</sup>

**N-(1,3-Dithiole-2-ylidene)thiobenzamides (5).** Two such compounds, *5a* and *5b*, prepared by reaction of 1-(diethylamino)propyne with a 5-aryl-1,2,4-dithiazole-3-thione, are described in Table 1. They form dark red or black crystals and are stable, contrary to the 1,3-oxathiole derivatives *4*; no decomposition is observed after several months at room temperature.

The structures of *5a* and *5b* have been studied by  $^1\text{H}$  NMR spectroscopy and mass spectrometry, and that of *5b* has been determined by X-ray diffraction.

**NMR Spectroscopy.**  $^1\text{H}$  NMR spectra of compounds *5*, given in Table 2, show the presence of only one chemical species, and low temperature ( $-80^\circ\text{C}$ ) measurements failed to show any modification of the NMR spectra. NMR has already given similar evidence for various 2-thioacylimino-1,3-dithioles.<sup>4-6</sup> However, 2-thioacylmethylene-1,3-dithioles, when differently substituted in positions 4 and 5, are obtained as mixtures of the two isomers corresponding to the possible *E* and *Z* configurations of the juxtacyclic double bond.<sup>1,2,9</sup>

The fact that the NMR spectra of compounds *5* show the presence of only one chemical species may, as for compounds *4*, be accounted for in two quite different ways (Scheme 2): (a) either there is effectively only one configuration of the juxtacyclic double bond, formula *5u* with possible elements of *5v*, or (b) the juxtacyclic bond has only a low double bond character, enabling free rotation, formula *5w*.

The free-rotation hypothesis is supported by the fact that two identical substituents in positions 4 and 5 of 2-thioacylimino-1,3-dithioles, give the same NMR signal,<sup>6</sup> and low temperature ( $-60^\circ\text{C}$ ) NMR measurements show no modification of the spectra.

At this point, it should be mentioned that previous experiments generally concerned 2-thioacylimino-1,3-dithioles with electron-withdrawing substituents ( $\text{COOR}$ ,  $\text{CF}_3$ ) in positions 4 and 5.<sup>6</sup> The present compounds, however, have an electron-releasing substituent ( $\text{NEt}_2$ ) on the 1,3-dithiole ring.

**Mass spectrometry.** Notwithstanding the different stabilities of compounds *4* and *5*, their mass spectra are similar, *cf.* Table 3 where the most important fragments are given.

The main fragmentation mode is the cleavage of the molecular ion into a molecule of dithiazolethione and a molecular ion of the ynamine, and the latter gives the most intense peak of the spectrum for *5a* as well as *5b*. This mechanism is supported by the observations of the corresponding metastable ion. Furthermore, the easy opening of the 1,3-dithiole ring is consistent with the results from a study on the  $\alpha$ -(1,3-dithiole-2-ylidene)thioketones fragmentation.<sup>9-11</sup>

These facts support the 1,3-dithiole structure attributed to compounds *5* and eliminates the possibility of a 2+2 cycloaddition, followed by a rearrangement which would have led to a 3,3a $\lambda^4$ ,4-trithia-1-azapentalene.

Relative amounts of the dithiazolethione molecular ion are very low. Similarly, peaks given by the ions  $\text{Ar}-\text{SCN}^+$ , which are the most intense for dithiazolethiones *2*, are relatively small for compounds *5*. On the other hand, by comparison with the molecular ion of the dithiazolethiones *2*, the relative amount of the fragment  $\text{Ar}-\text{CS}^+$  is greater for compounds *5* than for the dithiazolethiones *2*.

The other main peaks given by a compound *5* are also found in the spectra of the starting ynamine and dithiazolethione, *cf.* Table 3. The spectra show the presence of  $\text{R}-\text{CS}^+$  fragments but in the case of compounds *5*, this does not help defining the *Z* or *E* configuration of the juxtacyclic double bond. This problem has been solved through an X-ray structure determination of compound *5b*, as described below.

**X-Ray structure analysis.** This study has been performed by one of us (A.H.) on compound *5b*. Fig. 1 shows the molecular structure from this study. The numbering of atoms is consistent with the numbering of atoms in Table 4. Some bond lengths and one interatomic contact distance are given in the Figure. For further details see Table 5.

All atoms in Fig. 1 except C(42), C(43), C(44), and C(45) lie essentially in the same plane (the A plane), *cf.* Table 5. The plane through C(4), C(42), and C(44) (the B plane) is

Table 4. Fractional atomic coordinates, and temperature parameters  $B_{eq}$  ( $\text{\AA}^2$ ) for sulfur, oxygen, nitrogen and carbon. The expression used is

$$B_{eq} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j. \text{ Standard deviations in parentheses.}$$

Atom	x	y	z	$B_{eq}$
S1)	-0.28281(22)	0.32072(8)	0.25319(14)	5.3(2)
S(3)	-0.13174(26)	0.42880(8)	0.41053(15)	6.9(2)
S(8)	-0.16775(25)	0.20149(8)	0.38855(16)	6.4(2)
O	0.4150(6)	0.1538(2)	0.9473(4)	7.1(4)
N(6)	-0.0533(7)	0.3147(3)	0.4919(4)	5.4(4)
N(41)	-0.3064(9)	0.5114(3)	0.2264(5)	7.0(4)
C(2)	-0.1452(8)	0.3478(3)	0.3975(5)	5.2(4)
C(4)	-0.2744(9)	0.4476(3)	0.2586(5)	5.9(4)
C(5)	-0.3396(9)	0.3970(3)	0.1909(6)	5.5(4)
C(7)	-0.0485(8)	0.2507(3)	0.4983(5)	5.0(4)
C(9)	0.5132(9)	0.1977(3)	1.0444(6)	5.5(4)
C(42)	-0.3809(17)	0.5501(4)	0.3066(8)	11.7(7)
C(43)	-0.5527(13)	0.5221(4)	0.3121(10)	11.4(7)
C(44)	-0.1400(18)	0.5482(4)	0.2148(8)	11.3(7)
C(45)	-0.0708(14)	0.5198(5)	0.1254(10)	12.3(7)
C(71)	0.0760(8)	0.2249(3)	0.6175(6)	4.6(4)
C(72)	0.1621(10)	0.2676(3)	0.7103(6)	5.9(4)
C(73)	0.2780(10)	0.2456(3)	0.8217(6)	5.9(4)
C(74)	0.3025(8)	0.1815(3)	0.8402(6)	5.6(4)
C(75)	0.2147(10)	0.1373(3)	0.7489(7)	6.7(5)
C(76)	0.1041(10)	0.1614(3)	0.6387(7)	6.2(4)
C(51)	-0.4632(9)	0.3987(3)	0.0568(5)	7.1(4)

almost perpendicular to the A plane; the dihedral angle is  $88^\circ$ . N(41) lies  $-0.41 \text{ \AA}$  from the B plane, and the amino group is thus pyramidal.

The juxtacyclic C(2)–N(6) bond of  $1.291(7) \text{ \AA}$  and the cyclic C(4)–C(5) bond of  $1.314(1) \text{ \AA}$  may be described as pure double bonds, and the C(7)–S(8) bond of  $1.664(6) \text{ \AA}$  is close to being a double bond.<sup>13</sup> The length of the N(6)–C(7) bond,  $1.339(8) \text{ \AA}$ , agrees with the length of the aromatic C–N bond,  $1.340 \text{ \AA}$ , in pyridine.<sup>14</sup> Thus C(7) participates in  $\pi$ -bonding with N(6) as well as with S(8).

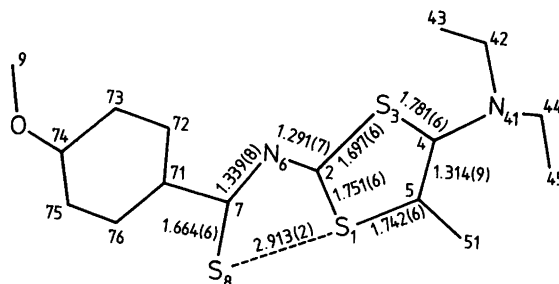
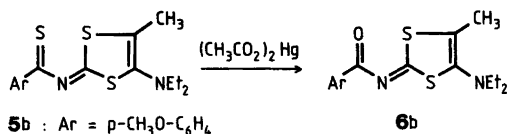


Fig. 1. The molecular structure of compound 5b with numbering of atoms. Bond lengths, and one intramolecular S...S distance, in the central ring system are given in  $\text{\AA}$  units. Standard deviations in parentheses.

Table 5. Bond lengths  $l(ij)$ , bond angles  $\angle(ijk)$ , and deviations  $\Delta j$  from least squares planes A and B. Standard deviations in parentheses.

Atoms			Bonds $l(ij)$ Å	Angles $(ijk)^\circ$	Deviations of atoms $j$ from planes	
$i$	$j$	$k$			$\Delta j(\text{A})$ Å	$\Delta j(\text{B})$ Å
C(5)	S(1)	C(2)	1.742(6)	95.1(3)	0.02	
C(4)	S(3)	C(2)	1.781(6)	97.6(3)	-0.05	
C(7)	S(8)		1.664(6)		-0.11	
C(74)	O	C(9)	1.390(7)	116.4(5)	0.06	
C(2)	N(6)	C(7)	1.291(7)	125.4(5)	-0.05	
C(4)	N(41)	C(44)	1.38(1)	113(1)	0.01	-0.41
C(42)	N(41)	C(4)	1.44(2)	118(1)		
C(44)	N(41)	C(42)	1.56(2)	106(1)		
S(3)	C(2)	S(1)	1.697(6)	114.1(4)	-0.04	
S(1)	C(2)	N(6)	1.751(6)	128.7(5)		
N(6)	C(2)	S(3)		117.3(5)		
C(5)	C(4)	N(41)		127.9(6)	0.02	0.00
C(5)	C(4)	S(3)		113.6(5)		
N(41)	C(4)	S(3)		118.4(5)		
C(4)	C(5)	S(1)	1.314(9)	119.6(5)	0.04	
C(51)	C(5)	C(4)	1.526(8)	125.0(6)		
C(51)	C(5)	S(1)		115.3(5)		
N(6)	C(7)	S(8)	1.339(8)	125.2(4)	-0.05	
S(8)	C(7)	C(71)		120.9(5)		
C(71)	C(7)	N(6)	1.504(8)	113.9(5)		
O	C(9)		1.458(8)		0.06	
N(41)	C(42)	C(43)		109.7(8)		0.00
C(42)	C(43)		1.50(2)			-0.49
N(41)	C(44)	C(45)		111(1)		0.00
C(44)	C(45)		1.38(2)			-0.51
C(7)	C(71)	C(72)		118.8(5)	-0.01	
C(76)	C(71)	C(7)	1.353(9)	122.5(5)		
C(72)	C(71)	C(76)	1.383(8)	118.7(6)		
C(71)	C(72)	C(73)		120.5(6)	-0.07	
C(72)	C(73)	C(74)	1.389(9)	119.3(6)	-0.04	
C(73)	C(74)	C(75)	1.361(9)	121.3(6)	0.02	
C(73)	C(74)	O		124.6(6)		
O	C(74)	C(75)		114.1(6)		
C(74)	C(75)	C(76)	1.397(9)	117.3(6)	0.05	
C(75)	C(76)	C(71)	1.378(9)	122.9(6)	0.05	
C(5)	C(51)				0.12	

This shows that the structure of compound **5b** is *5u*, cf. Scheme 2, possibly with some elements of *5v*, since the observed S(1)⋯S(8) distance of 2.913(2) Å may indicate some bonding interaction. It should be noted in this connection that the shortest distance found in a crystal between two sulfur atoms belonging to different molecules is 3.20 Å.<sup>15</sup> The observed S(1)⋯S(8) distance is compatible with similar results for related compounds.<sup>16</sup>



One may conclude that the formation of a strong juxtacyclic C–N double bond, which precludes a rotation around this bond, as well as a pronounced conjugation in the N(6)–C(7)–S(8) sequence, *cf.* Fig. 1, are decisive for the geometry of the C(2)–N(6)–C(7)–S(8) part of the molecule. The same seems warranted for compounds 4, and one may therefore expect that the structures of these are similar to those of compounds 5, namely 4*u* with some elements of 4*v*.

*N*-(1,3-Dithiole-2-ylidene)-*p*-methoxybenzamide 6*b*. When reacted with mercury(II) acetate, the thiobenzamide 5*b* yields the benzamide 6*b*, as shown in Scheme 3.

The IR spectrum of compound 6*b* does not contain any noticeable absorption band between 1650 and 1800 cm<sup>-1</sup>, a fact consistent with a significant interaction between the carbonyl oxygen and one of the sulfur atoms of the 1,3 dithiole ring as in the case of  $\alpha$ -(1,2-dithiole-3-ylidene)ketones.<sup>17</sup>

The <sup>1</sup>H NMR spectrum of benzamide 6*b*, in the presence of this(dipivaloylmethana-to)europium confirms the proximity of the carbonyl to the benzene ring, the largest modification of the chemical shifts affecting the two phenyl protons in position ortho relative to the carbonyl.

## EXPERIMENTAL

Melting points (uncorrected) have been determined with a heated sample Reichert microscope. Spectrometers used are: IR: Perkin Elmer 222; UV: Beckman Acta M–VI, with dioxane used as solvent; Mass: Varian Mat CH5 and Jeol JMS–D 300 (70 eV); NMR: Varian A-60 and Varian EM-360.

*Starting compounds.* 1,2,4-Dithiazole-3-ones:<sup>18</sup> 1*a* (5-Phenyl-); 1*b* (5-*p*-Methoxyphenyl-). 1,2,4-Dithiazole-3-thiones:<sup>18</sup> 2*a* (5-phenyl-); 2*b* (5-*p*-Methoxyphenyl-). 1-Diethylaminopropyne (Fluka): Mass spectrum: 111(100), 96(85), 72(18), 68(48), 58(62), 56(24), 55(29), 54(48), 44(65), 43(54), 42(24), 41(48). 1-Diethylamino-2-phenylacetylene:<sup>19</sup> Mass spectrum.<sup>20</sup>

*N*-(1,3-Oxathiole-2-ylidene)thiobenzamides 4. To a dithioazolone 1 (0.010 mol) dissolved in 100 ml of anhydrous diethyl ether, a solution of ynamine (0.012 mol) in the same solvent (15 ml) is slowly added. A red colour develops immediately. The mixture is stirred during one or two h at ordinary temperature and diethyl ether is eliminated without heating under reduced pressure.

The residue is recrystallised in ethanol. Compounds 4 obtained in this way are given in Table 1 with their UV spectra. <sup>1</sup>H NMR spectra are given in Table 2.

*N*-(1,3-Dithiole-2-ylidene)thiobenzamides 5. To a dithiazolethione 2 (0.01 mol) dissolved in 100 ml of anhydrous xylene, a solution of ynamine (0.02 mol) in the same solvent (10 ml) is slowly added. The colour changes immediately from yellow to red. The reaction is followed by thin-layer chromatography.

Heating under reflux is sometimes necessary if some dithiazolethione remains after one hour stirring at ordinary temperature. The xylene is removed under reduced pressure and the residue, dissolved in benzene, is chromatographed on alumina, the elution being made with light petroleum.

Compounds 5 obtained in this way, with their UV spectra, are given in Table 1. Corresponding <sup>1</sup>H NMR spectra are given in Table 2.

*N*-(4-Diethylamino-5-methyl-1,3-dithiole-2-ylidene)-*p*-methoxybenzamide 6*b*. To the thiobenzamide 5*b* (0.014 mol) dissolved in the minimum amount of acetic acid, a solution obtained by dissolving 0.015 mol of mercury(II) oxide in 100 ml of acetic acid is progressively added. The mixture is heated ten minutes in a steam bath and then filtered in order to remove the mercury(II) sulfide. After addition of water, the benzamide 6*b* is extracted by benzene. The benzenic solution, dried with magnesium sulfate, is chromatographed on alumina, the elution being made with light petroleum. Benzamide 6*b* is a yellow oil.



IR spectrum between 1500 and 2000  $\text{cm}^{-1}$ ; (in KBr) 1512; 1576; 1605; 1616.5  $\text{cm}^{-1}$  – (in  $\text{C}_2\text{Cl}_2$ ) 1511.5; 1578.5; 1606; 1629  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS):  $\delta$  1.00 (6H, t,  $\text{CH}_3$  of  $\text{NEt}_2$ , 77 Hz), 2.20 (3H, s, 5- $\text{CH}_3$ ), 2.83 (4H, q,  $\text{CH}_2$  of  $\text{NEt}_2$ , 77 Hz), 3.80 (3H, s,  $\text{OCH}_3$ ), 6.88 and 8.24 (4H, qAB, 79 Hz, phenyl protons). After recording this spectrum, tris(dipivaloylmethanato)europium is added in molar amount  $\rho = [\text{Eu}]/[6b] = 0.25$ . A new recording shows that the largest variation of chemical shift  $\Delta\delta = 0.33$  ppm) concerns the protons nearest to the carbonyl in the *p*-methoxyphenyl group. Other variations are around 0.07 ppm.

*Structure analysis.* the crystals of *N*-(4-diethylamino-5-methyl-1,3-dithiole-2-ylidene)-*p*-methoxythiobenzamide **5b** are red prisms elongated along *a*.

Crystal data:

$\text{C}_{16}\text{H}_{20}\text{N}_2\text{OS}_3$ ; M.W. = 352.53

Space group  $P2_1/c$

$a = 10.967(6)$ ,  $b = 20.88(1)$ ,  $c = 7.941(6)$  Å

$\beta = 106.03(7)^\circ$

$V = 1747.5$  Å<sup>3</sup>

$Z = 4$

$D_c = 1.342$  g/cm<sup>3</sup>,  $D_m$  (flotation) = 1.35 g/cm<sup>3</sup>

$\mu$  (MoK $\alpha$ ) = 4.15  $\text{cm}^{-1}$

A crystal of approximate dimensions 0.5×0.5×0.2 mm was used for the X-ray analysis which was carried out on a computer-controlled Enraf-Nonius CAD4 diffractometer using graphite monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å).

The intensities of 2883 independent reflections within  $\theta = 25^\circ$  were measured at  $t = 20^\circ\text{C}$  by the  $\omega - 2\theta$  technique. Maximum scan time per reflection was set to 20 s, and the data set was collected within 30 h. Reflections for which  $I > 2\sigma(I)$  where  $\sigma(I)$  is based on counting statistics, were accepted as observed. By this criterion 1788 reflections were considered observed. Lp corrections were applied but absorption corrections were considered unnecessary.

The structure was solved by direct methods (MULTAN)<sup>21</sup> and refined by means of CRYLSQ of X-Ray-76<sup>22</sup> to an *R* of 0.050. The methyl hydrogens were found from difference maps and the positions of the others were calculated. All calculations were carried out on the CYBER 171 of the University of Tromsø.

The final atomic coordinates for S, O, N and C atoms are given in Table 4. Hydrogen positions, temperature parameters and structure factor lists are available on request (A.H.). Scattering factors given by Cromer and Mann were used for S, O, N and C.<sup>23</sup> For hydrogen, the scattering factor curve given by Stewart *et al.*<sup>24</sup> was used.

Fig. 1 shows the molecule with numbered atoms. Bond lengths and angles are given in Table 5. All bond lengths, except those of the diethylamino group, are found to be normal. The carbon atoms of the diethylamino group show pronounced anisotropic temperature parameters, probably due to some disorder, and the dimensions given for this part of the molecule are, due to this, probably less accurate than the standard deviations indicate. However, the possible disorder was difficult to resolve.

A least squares plane *A* for all non-hydrogen atoms except C(42), C(43), C(44) and C(45) and a plane *B* through C(4), C(42) and C(44) were calculated with equal weights. Deviations of atoms from these planes are given in Table 5.

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Received April 11, 1984.