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A NOVEL REARRANGEMENT REACTION OF 2,5,5-TRIARYL-2-THIAZOLIN-4-ONES DURING THIATION

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Abstract—2,5,5-Triphenyl-2-thiazolin-4-one (**7**) is transformed by P_2S_5 in boiling dioxane or xylene into N-(3-phenyl-2-benzo[b]thienyl)-thiobenzamide (**10**). The chloro substituted derivatives **16** and **17** of **7** react analogously but, in the case of **17**, a by-product which is believed to be the desired 2-thiazoline-4-thione **18** is also formed. The latter may be isomerised subsequently to **20**. The structure of **10** was elucidated mainly by mass spectrometry and X-ray. Various chemical transformations of **10** and its chloro substituted derivatives **19** and **20** are discussed.

Zusammenfassung—Beim Erhitzen mit Phosphorpentasulfid in Dioxan oder Xylol wird das 2,5,5-Triphenyl-2-thiazolinon-(4) (**7**) in N-(3-Phenyl-2-benzo[b]thienyl)-thiobenzamid (**10**) umgewandelt. Analog reagieren die Chlor-Substitutionsprodukte **16** und **17** von **7**, im letzteren Falle erhält man jedoch als Zweitprodukt eine mit dem gewünschten 2-Thiazolin-4-thion **18** höchstwahrscheinlich identische Verbindung, welche nachträglich zu **20** isomerisiert werden kann. Die Struktur **10** wurde in der Hauptsache aus dem Massenspektrum der Verbindung abgeleitet und auf Röntgen-strukturanalytischem Wege erhärtet. Verschiedene chemische Umwandlungen von **10** und seinen Chlor-Substitutionsprodukten **19** und **20** werden beschrieben.

In the preceding paper[1] the aluminium chloride induced desulfuration-rearrangement of 5,5-diphenyl-2,4-thiazolidinedithione (**1**) to 4,5-diphenyl-4-thiazoline-2-thione (**3**) was described. Since, in the related imidazole series, in addition to 5,5-diphenyldithiohydantoin (**2**) and its derivatives[2] diarilimidazolinethiones, e.g. **6**,[3] were also found to undergo similar reactions and to yield compounds **4** and **9**, respectively, we decided to study the behaviour of 2,5,5-triphenyl-2-thiazoline-4-thione (**5**) under the action of aluminium chloride.

The starting substance for the synthesis of **5**, the corresponding oxo derivative **7** was readily obtained by reacting α-chloro-α,α-diphenylacetic acid with thiobenzamide. IR, NMR and MS spectra, as well as chemical properties (Experimental) were all in good agreement with the assumed structure **7**. When, however, this substance was treated with phosphorus pentasulfide, an isomer (**A**) of the expected thioxo derivative **5** was obtained. This product contained, both according to its IR and NMR spectrum an NH group. The presence of an acidic proton in **A** was also revealed by the ability of **A** to undergo methylation when acted upon by methyl iodide in the presence of sodium methoxide. The monomethyl derivative **B** thus obtained proved to be an S- rather than an N-Me derivative since, on oxidative elimination of the S atom (see below), the Me group, too, is lost. Consequently the NH group of **A** forms part of an —NH—C(=S)— grouping which, when methylated, transforms into the —N=C(—SMe)— grouping of **B**. The presence of the thioamide moiety in **A** is corroborated by Raney-nickel desulfuration yielding compound **C** which contains, according to its NMR spectrum, an —N=CH— azomethine grouping. Finally, SeO_2 oxidation of both **A** and **B**, as well as Hg(II) acetate or hydrogen peroxide treat-

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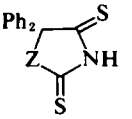
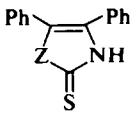
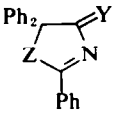


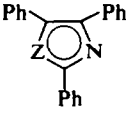
1: Z = S
2: Z = NH



3: Z = S
4: Z = NH



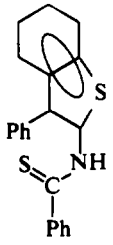
5: Z = Y = S
6: Z = MeN; Y = S
7: Z = S; Y = O



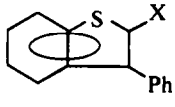
8: Z = S
9: Z = MeN

ment of A, furnish compound D, the oxo analogue of A which contains, according to its IR spectrum, an —NH—C(=O)— amide grouping. D is smoothly re-converted into A by phosphorus pentasulfide treatment.

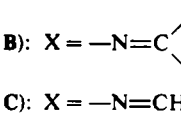
The appearance of an NH proton in the thiation product A of 7 necessitates the assumption that, in the course of the thiation, one of the phenyl rings was substituted and that the aromatic hydrogen thereby expelled became ultimately attached to the N atom. Since A is an isomer of the expected normal thiation product of 7, the substitution mentioned above into one of the phenyl rings has to be an intramolecular one and to lead to the formation of a new ring. Several alternative structures for A may be drawn on the basis of these considerations and one of these structures, 10, which may be deduced from 5 by closure of a thiophene ring and simultaneous opening of the original thiazole cycle, was, by examination of the MS spectrum of A (see below), proved to be correct. This structure assignment for A was corroborated also by X-ray (see below).



10



10 (= A): X = —NH—CS—Ph



11 (= B): X = —N=C(Ph)(SMe)

12 (= C): X = —N=CH—Ph
13 (= D): X = —NH—CO—Ph

†The same pattern of the aromatic proton signals was displayed also in the NMR spectra ($CDCl_3$) of compounds 7 and 17 (Experimental), 6 (*ortho* protons: 485–470, other aromatic protons: 465–430 Hz), the oxo analogue (Y = O)[3] of the latter (*ortho* protons: 480–465, other aromatic protons: 465–430 Hz) as well as of the oxazole analogue (Z = Y = O) of 7 (*ortho* protons: 8·4 δ, dd, $J = 8$ and 2 Hz, other aromatic protons: 470–430 Hz). No comparable deshielding effect of the C=S group on the *ortho* protons of the phenyl ring of the thiobenzoyl group was observed in the NMR spectra of the compounds 10, 19 and 20, and of the C=O group in the NMR spectrum of compound 13 either (Experimental). This may be a consequence of the non-planarity of the thiobenzoyl and benzoyl groups, respectively, proved—at least for the crystalline state—of compound 10 (see below).

A red oil was obtained as a by-product in the reaction of 7 with phosphorus pentasulphide. This resisted all attempts at crystallization and could be identical with the desired compound 5 (*cf* with the analogous result on thiation of compound 17).

Thiation of 7 was studied also under less vigorous conditions, *viz* in refluxing THF. At this temperature the reaction proceeded very slowly and yielded the same products, besides considerable amounts of unchanged starting material.

From structure 10 for the thiation product of 7 structures 11, 12 and 13 follow immediately for the methylation, desulfuration and oxidation products, respectively, of the former, all these structure assignments being corroborated by the mass spectra (see below) of these compounds.

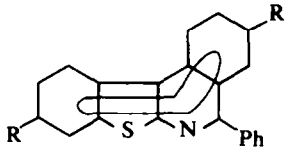
When compound 10 was reacted with anhydrous $AlCl_3$ in boiling toluene, 1 mole of H_2S was eliminated. The product obtained proved to be very stable under electron impact and the fully aromatic structure 14 was therefore assigned to it.

In addition to 7 its 2-(*p*-chlorophenyl) and 5,5-bis-(*p*-chlorophenyl) analogues 16 and 17, respectively, were also reacted with phosphorus pentasulfide to yield the corresponding chloro derivatives 19 and 20 of 10. 20 was S-methylated to 21, and both 20 and 21 gave 15 on treatment with aluminium chloride in toluene.

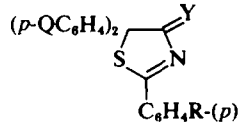
In the reaction 17 to 20 a red crystalline by-product, apparently corresponding to the oily by-product obtained in the course of thiation of 7, was also formed. Since the IR spectrum of this by-product does not contain an Amide I band and in its NMR spectrum the characteristic pattern of the aromatic proton signals of 17 (doublet of doublets of two *ortho* protons downfield to the multiplet of the remaining 11 aromatic protons) is retained,† the red compound is thought to be identical with the desired thioxo analogue 18 of 17.

When treated with phosphorus pentasulfide in boiling xylene, 18 is isomerised into 20. The presence of phosphorus pentasulfide is essential for this isomerization to occur since 18 does not change even on prolonged refluxing with pure xylene. Reaction 18 → 20 seems, at least on the preparative scale, to be slower than reaction 17 → 20. Consequently, 18 (if at all) is not the only intermediate of the latter reaction.

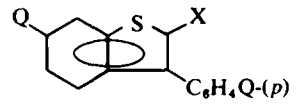
Isomerization of 18 into 20 may be achieved also by aluminium chloride in boiling xylene; under these conditions, however, part of compound 20 becomes transformed, as expected, into 15. No 4,5-bis(*p*-chlorophenyl)-2-phenylthiazole (22)



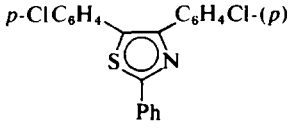
14: R = H
15: R = Cl



16: Q = H, R = Cl, Y = O
17: Q = Cl, R = H, Y = O
18: Q = Cl, R = H, Y = S



19: Q = H, X = —NH—CS—C_6H_4Cl-p
20: Q = Cl, X = —NH—CS—Ph
21: Q = Cl, X = —N=C(SMe)—Ph



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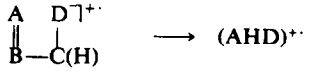
could be isolated from the reaction; thus, the reactivity of **18** towards aluminium chloride differs considerably from that of the corresponding imidazolinethiones (e.g. **6**).

Mass spectrometry

The mass spectrum of compound **10** (Fig 1) shows only four abundant ions at *m/e* 345 (M), 312 (M-H), 242 (M-PhC≡N) and 121 (Ph-C≡$S^{\oplus}$), and four less intensive peaks at *m/e* 223 (M-PhCS-H), 165 ($C_{13}H_9^{\oplus}$), 104 (Ph-C≡$NH^{\oplus}$) and 77 ($Ph^{\oplus}$), the formation of which can be rationalized as follows.

The base peak of the spectrum at *m/e* = 121 arises from the $PhCS^+$ ion, which is known to be the most abundant in the mass spectra of thiobenzoates.[4] Further loss of CS from this ion, accompanied by a metastable ion at m* = 49·1, gives ion *m/e* = 77. The *m/e* = 165 ion is reported to appear in the spectrum of 3-phenyl-benzo[b]-thiophene[5b] as well as in other phenyl-substituted condensed 5-ring heterocycles.[5a] Formation of the ion *m/e* = 312 may most easily be explained by assuming loss of ·SH from the tautomeric thioimidic acid form of **10**. A metastable peak, due to this transition, occurs at m* = 283.

The most interesting feature in the spectrum of compound **10** is the formation of the *m/e* = 242 ion. Theoretically it could not be excluded that this peak derives from a possible thermal rearrangement[6] but its relative intensity showed no evaporation temperature-dependence. Skeletal rearrangements upon electron impact in similar types of compounds were described and commented upon earlier.[4,7-9] They are assumed to proceed *via* a four-membered ring transition state if certain conditions are satisfied.[9] It is also known that if in the general formula



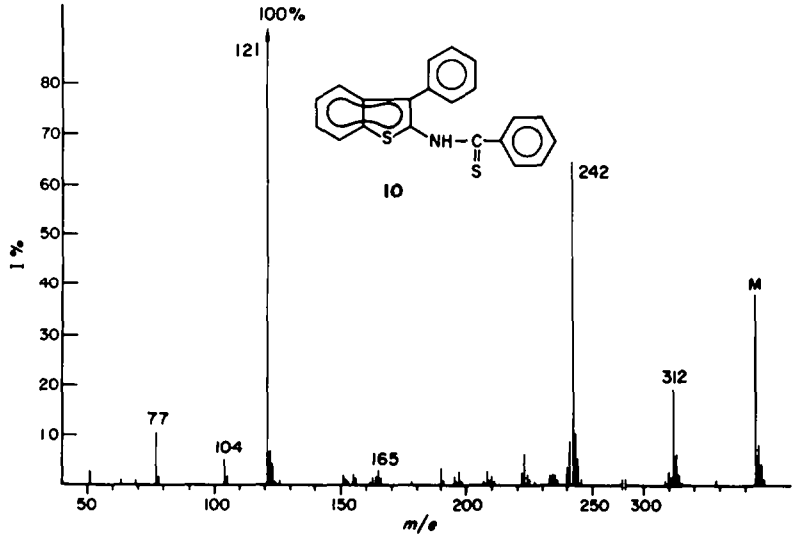
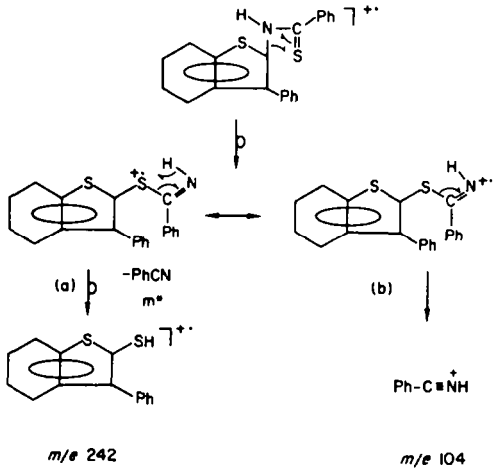


Fig 1. Mass spectrum of compound **10**.

C bears a hydrogen atom, both hydrogen- and skeletal rearrangements occur.[9a,b]

In terms of the above generalisation the rearrangement leading to the formation of ion $m/e = 242$ in the spectrum of **10** may be depicted as shown in Scheme 1 (Path a). By using the defocussing technique,† there appeared only one metastable peak at mass number 242, corresponding to the transition $M \rightarrow m/e = 242$.

The rearrangement-ion $m/e = 242$ furnishes the second most intense peak in the spectrum of **10**, whilst in the spectrum (Fig 4) of the C=O analogue **13** the corresponding $m/e = 226$ ion possesses only 1% intensity. This clearly shows the role of the heteroatoms involved in this rearrangement.



SCHEME 1

It is still a matter of discussion whether the tautomeric forms of the groups taking part in the 4-centre rearrangement need or need not to be invoked when explaining its mechanism.[9b] Although, as shown by the formation of the $(M—SH)^+$ ion, the tautomeric thioimidic acid form of **10** does exist under the conditions of the rearrangement, according to our opinion it need not be involved into the rearrangement process. This assumption is supported by the lack of any rearranged ion of this type in the spectrum (Fig 2) of the S-methyl derivative **11** which has the fixed thioimidate structure. Furthermore, another product of the rearranged molecular ion is the $Ph\text{-}C{\equiv}N^{\oplus}—H$ ion (m/e 104), see Scheme 1, Path b, which proves that the initial rearrangement process involves migration of the heteroaromatic group rather than that of an H atom. However, further studies will be needed in order to settle this problem.

The mass spectrum of **11** (Fig 2) shows only two abundant peaks, due to the molecular-ion ($M = 359$) and to the loss of the MeS· radical (m/e 312), respectively, which also confirm the structure given.

The mass spectrum of **12** (Fig 3) indicates the presence of an anil structure ($M = 313$) with the typical[10] fragmentations M—H ($m/e = 312$) and M—Ph ($m/e = 236$), respectively, from the azomethine group. These are accompanied by metastable ions at $m^* = 311$ and $m^* = 178$, respectively.

In the mass spectrum of **13** (Fig 4), apart from the molecular-ion, only the two peaks related to the benzoyl group exceed 10% relative intensity. This is in accordance with the published mass spectral behaviour of N-arylbenzamides[11] and of 2-thienyl benzoate.[12] The loss of CO from the benzoyl ion

†Acceleration voltage defocussing was used. The measured ratio of voltages was 1,429 (345/242 = 1,425).

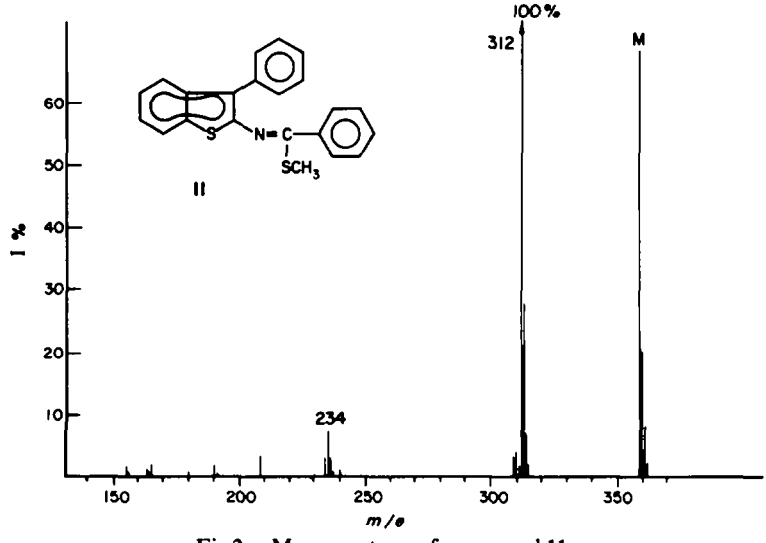


Fig 2. Mass spectrum of compound **11**.

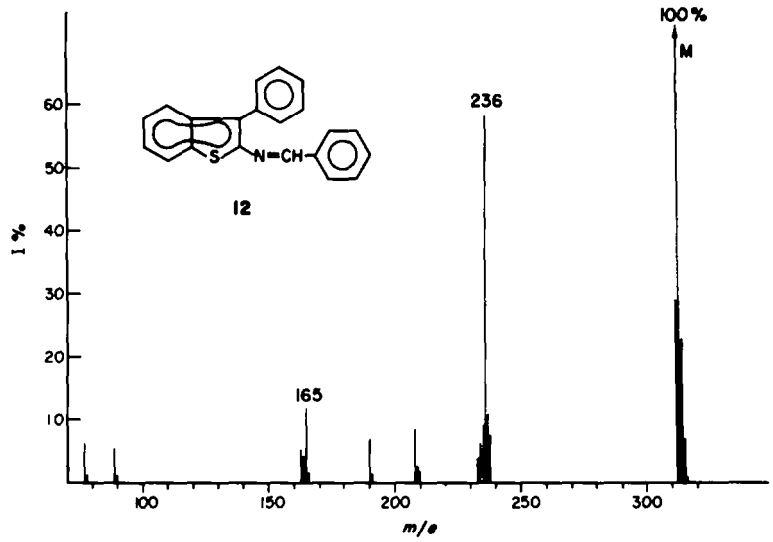


Fig 3. Mass spectrum of compound 12.

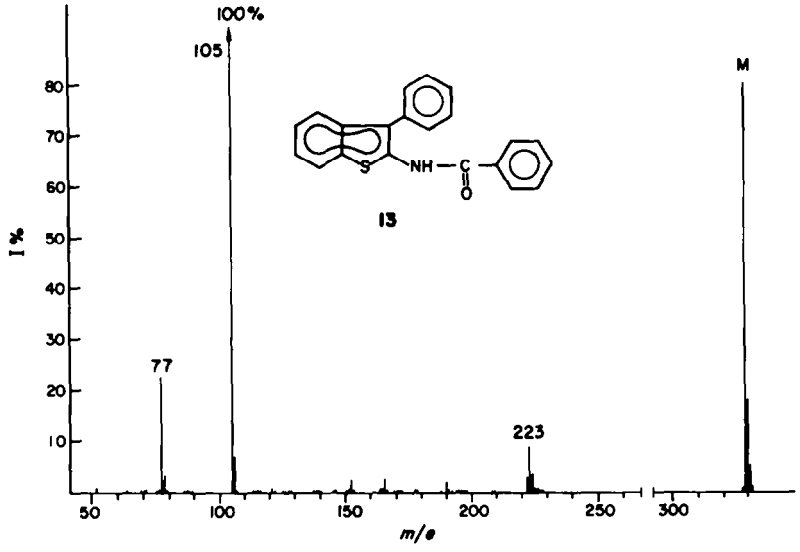


Fig 4. Mass spectrum of compound 13.

$m/e = 105$, yielding ion $m/e = 77$ is accompanied by a metastable ion at $m^* = 56{\cdot}4$. Loss of the benzoyl group from the molecular-ion gives ion $m/e = 224$. Further loss of hydrogen from this ion yields ion m/e 223; a metastable ion due to this transition appears at $m^* = 222$. High resolution mass measurement gave elemental composition $C_{14}H_9NS$ for ion $m/e = 223$.† The structure of this ion may be best represented by formula **23**. Further loss of H· and of CHN from **22** yields ions $m/e = 222$ and $m/e = 196$, respectively.

†The difference between the measured and calculated masses was 2·6 ppm.

The mass spectrum of **14** (Fig 5) reveals the presence of a fully aromatic system. The only peaks appearing are due to the molecular-ion (M = 311), to the ions formed by consecutive loss of hydrogens and to the doubly charged species of the former. The loss of H atoms is accompanied by a range of metastable ions between $m^* = 307$ and 311.

The mass spectrum of **18** has five prominent peaks at m/e 413 (M, 100%), 246 (41%), 176 (14%), 121 (13·5%) and 77 (6·5%), respectively. The m/e 246 ion has the elemental composition $C_{14}H_8Cl_2$ and, probably, the structure **24**; elimination of two chlorine atoms furnishes ion m/e 176 ($C_{14}H_8$). The ions m/e 121 and 77 are, of course, the thiobenzoyl

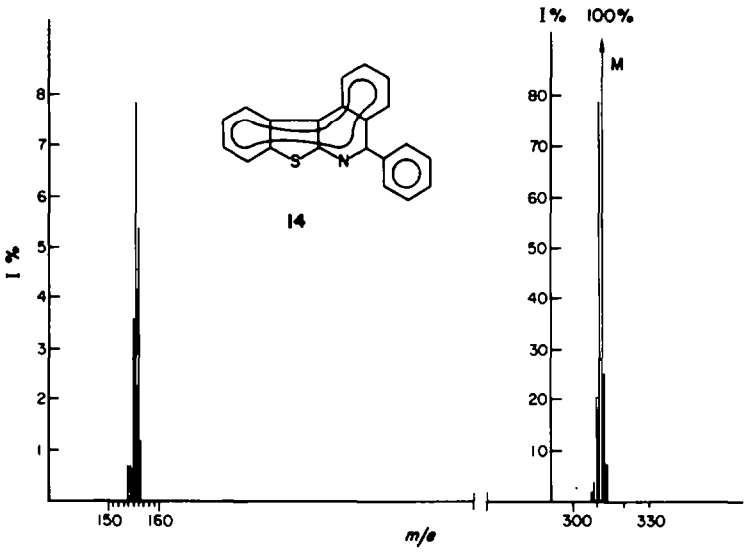
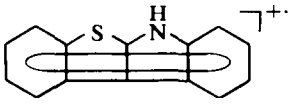


Fig 5. Mass spectrum of compound **14**.



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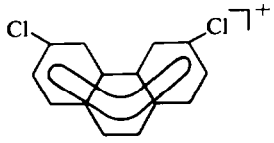

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and the phenyl ions, the intensity of the former being considerably reduced as compared to the mass spectrum of compound **10**.

X-Ray determination of the molecular structure of N-(3-*phenyl*-2-*benzo*[b]*thienyl*) *thiobenzamide* (**10**)

Fig 6 shows an ORTEP plot of the structure computed from the final positional and anisotropic thermal parameters of the non-hydrogen atoms given in Table 1 by the program of Johnson.[13]

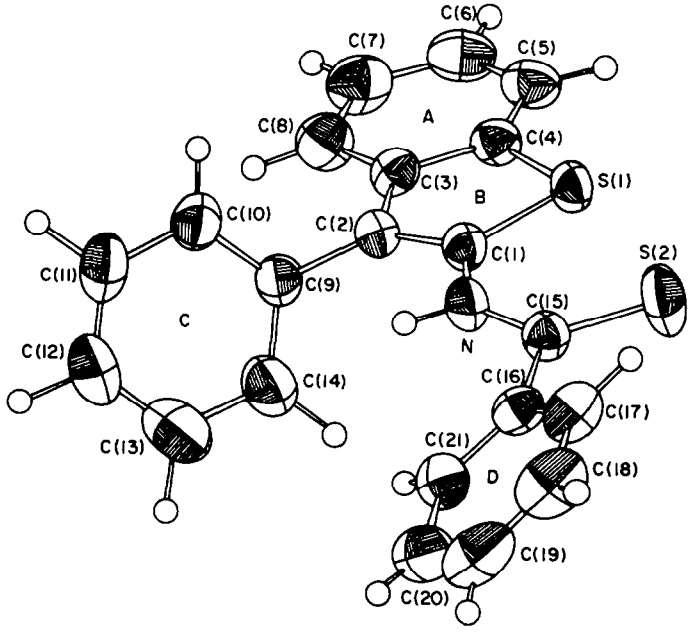

Fig 6. Molecular conformation of compound **10** in the crystalline state showing atomic and ring numbering used and the anisotropic thermal ellipsoids for the non-hydrogen atoms.

Table 1. Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms. Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form: $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S (1)	3496 (1)	2036 (1)	−0064 (1)	140 (1)	120 (1)	075 (1)	112 (1)	023 (1)	095 (1)
S (2)	3130 (1)	5027 (1)	2078 (1)	288 (2)	174 (1)	065 (1)	211 (1)	−013 (2)	072 (1)
N	2831 (3)	4473 (2)	−0495 (2)	150 (4)	102 (2)	068 (2)	085 (5)	016 (4)	071 (3)
C (1)	3034 (3)	2978 (3)	−1031 (3)	108 (4)	105 (3)	073 (2)	072 (5)	025 (5)	083 (4)
C (2)	2866 (3)	2137 (3)	−2365 (3)	108 (4)	127 (3)	079 (2)	078 (5)	020 (5)	098 (4)
C (3)	3114 (3)	0638 (3)	−2668 (3)	111 (4)	116 (3)	082 (2)	074 (6)	032 (5)	064 (4)
C (4)	3456 (3)	0420 (3)	−1513 (3)	112 (4)	111 (3)	103 (3)	090 (5)	034 (5)	095 (4)
C (5)	3690 (4)	−0973 (3)	−1556 (3)	125 (4)	136 (3)	144 (3)	119 (6)	043 (6)	142 (5)
C (6)	3609 (4)	−2133 (4)	−2791 (4)	155 (5)	135 (4)	169 (4)	141 (6)	035 (8)	095 (6)
C (7)	3286 (4)	−1928 (4)	−3954 (4)	174 (5)	140 (4)	129 (4)	128 (7)	038 (8)	022 (7)
C (8)	3034 (4)	−0573 (4)	−3913 (3)	160 (5)	144 (4)	102 (3)	117 (7)	017 (7)	044 (6)
C (9)	2411 (3)	2684 (3)	−3375 (3)	121 (4)	114 (3)	072 (2)	070 (6)	008 (5)	070 (4)
C (10)	3364 (4)	2959 (4)	−4307 (3)	176 (5)	184 (4)	101 (3)	163 (7)	075 (6)	146 (5)
C (11)	2905 (5)	3449 (4)	−5253 (3)	240 (6)	177 (4)	092 (3)	147 (8)	069 (7)	132 (5)
C (12)	1512 (5)	3639 (4)	−5281 (3)	232 (6)	189 (4)	110 (3)	109 (8)	−036 (7)	156 (5)
C (13)	0558 (5)	3456 (5)	−4311 (4)	179 (6)	243 (5)	190 (4)	125 (9)	−037 (8)	216 (7)
C (14)	1003 (4)	2955 (4)	−3361 (3)	158 (6)	219 (4)	136 (3)	090 (8)	000 (7)	202 (5)
C (15)	2759 (3)	5404 (3)	0774 (3)	112 (4)	110 (3)	081 (2)	063 (6)	017 (5)	067 (4)
C (16)	2263 (3)	6800 (3)	0915 (3)	105 (4)	108 (3)	098 (3)	040 (6)	048 (5)	087 (4)
C (17)	2813 (4)	8169 (4)	2027 (3)	162 (5)	117 (4)	113 (3)	048 (7)	057 (7)	052 (6)
C (18)	2290 (5)	9440 (4)	2205 (4)	230 (7)	117 (4)	172 (4)	090 (8)	116 (9)	098 (7)
C (19)	1223 (5)	9364 (4)	1316 (4)	247 (6)	133 (3)	209 (4)	191 (7)	233 (8)	199 (6)
C (20)	0676 (4)	8032 (4)	0222 (4)	169 (5)	189 (4)	173 (3)	142 (7)	097 (7)	237 (5)
C (21)	1204 (4)	6747 (3)	0005 (3)	140 (5)	122 (3)	120 (3)	071 (6)	049 (7)	142 (4)

Parameters for H atoms along with the C—H and N—H distances are shown in Table 2. The interatomic distances and bond angles together with their estimated standard deviations are presented in Table 3.

The average values found for the C—C bond lengths without thermal correction in the 6-membered rings, *A*, *C* and *D* are 1·388 (5), 1·380 (5) and 1·378 (5) Å, respectively, which are, therefore, somewhat less [$< 3\sigma_{av}$] than the C—C bond length of 1·392 (4) in crystalline benzene.[14] Bond lengths in the 5-membered ring, B are comparable with the corresponding data measured in thiophene.[15] The C(1)–C(2) distance of 1·354 Å is somewhat larger than in thiophene (1·342 Å). The C(2)–C(3) distance is almost the same as in thiophene, 1·435 Å. The S(11)–C(sp^2) distances, 1·739 and 1·742 Å, with a π-bond order of about 0·50[16] agree well, within the experimental error, with the theoretical value of 1·75 Å, given by Truter[17] and with the value of 1·735 Å found for thiophene, as well as with the average of 1·733 Å observed in the sulphathiazole polymorphs.[18]

The benzo[b]thiophene ring holds a phenyl (*C*) and a thiobenzamide group at a distance of 1·486 and 1·399 Å, respectively, of which the former corresponds to the single bond between C(sp^2)–C(sp^2) atoms. The latter, however, indicates a significant interaction between the thiophene ring *B* and the lone pair of the N atom forming a stronger multiple bond than that of 1·445 (10) Å found recently[19] between the phenyl ring and the sp^2/sp^3 N atom in 4-phenylthiosemicarbazide. Bond lengths in the thiobenzamide group can be compared to those of the 2-pyridinecarbothioamide[20] and benzamide[21] molecules, *viz.* S=C: 1·657 (4), C—N: 1·325 (4) and 1·342 (3) Å, respectively. The H atom, located unambiguously in the difference Fourier map, is at a distance of 0·94 (4) Å (*cf* 0·94 (4) Å given by Braibanti *et al.*[22]) from the N atom. The

Table 2. Fractional coordinates ($\times 10^3$), isotropic temperature factors (Å^2) and bond distances (Å) for the hydrogen atoms

	x/a	y/b	z/c	Bi	X–H distances*
H (5)	391 (4)	−106 (4)	−70 (4)	3·90	0·99 (4)
H (6)	377 (4)	−312 (3)	−278 (3)	2·28	1·00 (3)
H (7)	325 (4)	−277 (4)	−479 (4)	4·42	0·96 (4)
H (8)	273 (4)	−44 (4)	−474 (4)	3·96	1·00 (3)
H (10)	432 (4)	274 (4)	−438 (4)	4·48	0·95 (4)
H (11)	359 (4)	358 (4)	−601 (4)	4·28	1·05 (4)
H (12)	118 (5)	397 (4)	−605 (4)	4·75	1·07 (4)
H (13)	−57 (5)	356 (5)	−439 (5)	6·52	1·08 (5)
H (14)	21 (5)	274 (5)	−262 (4)	5·27	1·11 (4)
H (17)	356 (4)	806 (4)	266 (3)	3·05	1·03 (4)
H (18)	259 (6)	39 (6)	280 (5)	7·53	0·88 (6)
H (19)	78 (6)	29 (6)	150 (5)	7·68	1·02 (5)
H (20)	8 (5)	796 (5)	−37 (4)	4·85	0·82 (5)
H (21)	80 (4)	578 (4)	−77 (3)	3·22	0·98 (4)
H (N)	273 (4)	490 (4)	−112 (4)	3·45	0·94 (4)

*Where X = C(5 − 21) and N atoms

Table 3. Interatomic distances and bond angles with their e.s.d.'s

S(1)-C(1)	1·739 (3) Å	S(1)-C(4)-C(3)	112·31 (23)°
S(1)-C(4)	1·742 (3)	S(1)-C(4)-C(5)	125·49 (23)
C(1)-N	1·399 (4)	C(3)-C(4)-C(5)	122·18 (29)
C(1)-C(2)	1·354 (4)	C(4)-C(5)-C(6)	117·61 (31)
C(2)-C(3)	1·435 (4)	C(5)-C(6)-C(7)	120·95 (35)
C(3)-C(4)	1·396 (4)	C(6)-C(7)-C(8)	121·51 (36)
C(3)-C(8)	1·402 (5)	C(3)-C(8)-C(7)	119·01 (33)
C(4)-C(5)	1·397 (5)	C(2)-C(3)-C(4)	111·92 (26)
C(5)-C(6)	1·373 (5)	C(2)-C(3)-C(8)	129·35 (29)
C(6)-C(7)	1·393 (5)	C(4)-C(3)-C(8)	118·72 (28)
C(7)-C(8)	1·369 (5)	C(1)-C(2)-C(3)	111·63 (26)
C(2)-C(9)	1·486 (4)	C(1)-C(2)-C(9)	123·65 (26)
		C(3)-C(2)-C(9)	124·67 (26)
C(9)-C(10)	1·378 (5)	C(2)-C(9)-C(10)	121·57 (28)
C(9)-C(14)	1·389 (5)	C(2)-C(9)-C(14)	119·20 (28)
C(10)-C(11)	1·389 (5)	C(10)-C(9)-C(14)	119·22 (30)
C(11)-C(12)	1·348 (5)	C(9)-C(10)-C(11)	120·50 (32)
C(12)-C(13)	1·385 (6)	C(10)-C(11)-C(12)	120·24 (35)
C(13)-C(14)	1·395 (6)	C(11)-C(12)-C(13)	120·58 (37)
		C(12)-C(13)-C(14)	119·53 (39)
S(2)-C(15)	1·643 (3)	C(9)-C(14)-C(13)	119·74 (35)
C(15)-N	1·341 (4)		
C(15)-C(16)	1·484 (4)	C(1)-N-C(15)	130·91 (25)
C(16)-C(17)	1·398 (5)	S(2)-C(15)-N	123·66 (23)
C(16)-C(21)	1·382 (4)	S(2)-C(15)-C(16)	122·01 (23)
C(17)-C(18)	1·376 (6)	N-C(15)-C(16)	114·29 (26)
C(18)-C(19)	1·363 (6)	C(15)-C(16)-C(17)	119·36 (28)
C(19)-C(20)	1·369 (5)	C(15)-C(16)-C(21)	121·16 (27)
C(20)-C(21)	1·383 (5)	C(17)-C(16)-C(21)	119·39 (29)
		C(16)-C(17)-C(18)	119·69 (33)
S(1)-C(1)-N	123·64 (21)°	C(17)-C(18)-C(19)	120·38 (38)
S(1)-^{1}C(1)-^{3}C(2)	114·41 (22)	C(18)-C(19)-C(20)	120·53 (37)
C(2)-C(1)-N	121·95 (26)	C(19)-C(20)-C(21)	120·22 (34)
C(1)-S(1)-C(4)	89·73 (14)	C(16)-C(21)-C(20)	119·76 (30)

bond angles throughout the structure agree well with the corresponding data reported in the literature, *cf* e.g. the C-C(S)-N angle of 114·3 (3)° to those of 113·9 (3)° in 2-pyridinecarbothioamide and 113·4 (4)° in 4-phenylthiosemicarbazide.

The benzo[b]thiophene group is nearly planar; more strictly the C(1) and C(2) atoms deviate by −0·04 Å from the best plane defined by the benzene C atoms [0·911X + 0·407Y − 0·067Z − 3·286 = 0] while S(1) lies in it. The dihedral angle between the best plane of the benzo[b]-thiophene group and that of the phenyl ring *C* [0·130X + 0·779Y + 0·613Z − 1·173 = 0] is 66·8°. The least-squares plane of the thioamide moiety [0·850X + 0·526Y + 0·040Z − 3·575 = 0] makes an angle of 9·8° with the plane of the benzo[b]thiophene group and it is tilted to the plane of the phenyl ring *D* [0·647X + 0·552Y − 0·526Z − 3·122 = 0] by an angle of 35·1°. The dihedral angle between the best planes of the phenyl rings *C* and *D* is 79·0°. The full conformation of the molecule, in agreement with the remarks given above can be seen well in Fig 6.

EXPERIMENTAL

Synthesis of 2,5,5-triaryl-2-thiazolin-4-ones

(a) A mixture of α-chloro-α,α-diphenylacetic acid (12·3 g; 50 mmoles), thiobenzamide (6·8 g; 50 mmoles), AcOH (50 ml) and Ac_2O (5 ml) was refluxed for 30 min to yield 13·7 g (83%) of the colourless crystals of **7**, m.p. 154–6° (EtOH).

The molecular formula, $C_{21}H_{15}NOS$ was established by high resolution mass spectrometry.† The mass spectrum contained abundant ions at *m/e* 329 (M, 60%), 287 (22%), 198 (37%), 166 (49%) 165 (base peak) and 121 (38%) corresponding to $M^{\oplus}$, M-NCO, $Ph_2C{=}S^{\oplus}$, $C_{13}H_9^{\oplus}$ and $Ph\text{-}C{\equiv}S^{\oplus}$, respectively, in good agreement with structure **7**; IR (KBr): Amide I 1720 cm^{-1}; NMR ($CDCl_3$): 500–485 Hz (m) and 460–435 Hz (m), intensity ratio 2:13, ArH; UV (EtOH): 282 (4·36), 325 (3·50) sh.

(b) Compound **16** was prepared analogously in 83% yield, m.p.: 191–3° from EtOH or AcOH. (Found: Cl, 9·50; N, 4·05; S, 9·01. Calcd. for $C_{21}H_{14}ClNOS$ (363·86): Cl, 9·75; N, 3·85; S, 8·82%).

(c) *p,p'*-Dichlorobenzilic acid was transformed with $POCl_3$ into α-chloro-α,α-di(*p*-chlorophenyl)-acetic acid and the crude gummy product obtained was reacted without further purification with thiobenzamide as de-

†Thanks are due to Dr. J. Møller, The H. C. Ørsted Institute, Copenhagen, for running the mass spectrum of this compound.

scribed under (a) to yield 66% of **17**, colourless crystals, m.p. 165–7° from EtOH (Found: N, 3·60; S, 8·61. Calcd. for $C_{21}H_{13}Cl_2NOS$ (398·30); N, 3·52; S, 8·05%); IR(KBr): Amide I 1720 cm^{-1}; NMR ($CDCl_3$): 500–486 Hz (dd) and 468–440 Hz (m), intensity ratio 2:11, ArH.

Raney nickel desulfuration of **7**

A mixture of **7** (0·8g; 2·5 mmoles), Raney Ni (4·0 g), 5% $NaHCO_3$ aq (5 ml) and dioxane (20 ml) was refluxed for 4 hr; the catalyst was removed, part of the solvent was distilled off and the soln was diluted with water to yield 0·3 g of a colourless ppt which by its IR spectrum and TLC, proved to be identical with α,α-diphenylacetamide. When the aqueous alkaline mother liquor was acidified, another crop (0·2 g) of colourless crystals was precipitated, m.p. 144–146° (aqueous EtOH) which by IR spectrum and TLC were shown to be identical with α,α-diphenylacetic acid.

Synthesis of N-(3-*aryl*-2-*benzo*[b]*thienyl*)-*thiobenzamides*

(a) A mixture of **7** (16·5 g; 50 mmoles), P_2S_5 (10 g; 50 mmoles) and xylene (120 ml) was refluxed for 3 hr. After cooling, about 4 times its volume of light petroleum was added to the resulting mixture. The crystalline ppt was washed thoroughly with light petroleum, dried, triturated with 5% $NaHCO_3$ aq, allowed to stand with this soln overnight, filtered off, washed with water and recrystallized from 1-BuOH (about 200 ml) to yield 7·4 g (44%) of yellow crystals of **10**, m.p.: 193–4° (EtOH–benzene).

The molecular formula, $C_{21}H_{15}NS_2$ of the product was established by high resolution mass spectrometry; †IR (KBr): νNH 3350 cm^{-1}; NMR ($CDCl_3$) NH 9·98 (b), ArH 480–432 Hz, m; UV (EtOH): 224 (4·51); 231 (4·53); 254 (4·33), sh.; 372 (3·81).

(b) The same product was obtained when the reaction was performed in boiling dioxane. The butanol mother liquor of the first recrystallization was evaporated to dryness *in vacuo* and the residue was extracted with boiling gasoline. (The insoluble red gum contained, according to TLC, mainly **10**, and phosphorus derivatives.) On cooling, orange coloured crystals, consisting according to TLC mainly from unreacted **7**, were deposited from the gasoline soln. The mother liquor of the crystals was again evaporated to dryness. The residue was worked up by preparative TLC (adsorbent: Kieselgel G; application in $CHCl_3$ soln; development: benzene-cyclohexane, 1:1); the component of highest migration speed was eluted with ether. Evaporation of the solvent furnished an orange coloured oil which did not crystallize.

(c) When the reaction was performed by refluxing the soln of the reactants for 40 hr in dry THF and the oily dry residue was worked up by triturating it with 5% $NaHCO_3$ aq, crystals of unchanged starting material were obtained. The aqueous layer was extracted with chloroform, dried and analysed by TLC as described above; three components: a further amount of unchanged **7**, **10** and the orange red oily by-product could only be detected.

(d) Compound **16** was reacted with P_2S_5 as described under (a) to yield 30% of **19**, orange-yellow crystals, m.p. 152–4° from AcOH. (Found: Cl, 9·36; N, 3·78; S, 16·51. Calcd. for $C_{21}H_{14}ClNS_2$ (379·92): Cl, 9·33; N, 3·69; S, 16·68%); IR (KBr): νNH 3340 cm^{-1}; NMR ($CDCl_3$): NH 9·65δ, ArH 470–420 Hz, intensity ratio 1:13; UV (EtOH): 228 (4·50); 264 (4·34), sh; 376 (3·73).

(e) A mixture of **17** (2·0 g; 5 mmoles), P_2S_5 (1·1 g; 5 mmoles) and anhyd dioxane (15 ml) was refluxed for 5 hr, filtered hot and evaporated to dryness. The residue was recrystallized from EtOH and the red crystalline product was triturated with 10% NaOH aq and washed with water. The red crystalline product (1·6 g) thus obtained was, according to its m.p. (132–43°) inhomogeneous. Recrystallization from gasoline and three subsequent recrystallizations from 1-propanol furnished the yellow crystals of **20**, m.p. 232–3°. (Found: Cl, 17·07; N, 3·41; S, 15·66. Calcd. for $C_{21}H_{13}Cl_2N_2S_2$ (414·36): Cl, 17·11; N, 3·38; S, 15·48%); IR (KBr): νNH 3360/3340 (d); NMR ($CDCl_3$): NH 9·68, ArH 474–432 Hz.

5,5-*Di*(p-*chlorophenyl*)-2-*phenyl*-2-*thiazoline*-4-*thione* (**18**)

The orange product (a mixture, according to TLC, of compounds **18** and **20**) obtained by P_2S_5 treatment of **17** as described above under (e) and subsequent recrystallization from 1-propanol (1·15 g; 54%; m.p. 150–152°) was worked up by preparative TLC (adsorbent: Kieselgel G, Merck, development: benzene–cyclohexane, 2:8, elution ether) and compound **18**, obtained by evaporation of its ethereal soln, was recrystallised from aq EtOH to yield red crystals of m.p. 153–154°. (Found: Cl, 17·14; N, 3·42; S, 15·02. Calcd. for $C_{21}H_{13}Cl_2NS_2$ (414·36): Cl, 17·11; N, 3·38; S, 15·48%); IR (KBr): *No* NH band; NMR ($CDCl_3$): 480–463 Hz (dd) and 455–428 Hz (m), intensity ratio 2:11, ArH; no H exchangable with D_2O.

Isomerisation of 5,5,5-*bis*(p-*chlorophenyl*)-2-*phenyl*-2-*thiazoline*-4-*thione* (**18**)

A mixture of **18** (130 mg), P_2S_5 (100 mg) and dry xylene (10 ml) was refluxed for 15 hr. According to TLC, small amounts of the isomeric **20** were present in the mixture already after 1 hr, but the starting compound was not completely isomerized even after 15 hr. The mixture was evaporated to dryness, the residue was triturated with light petroleum and, subsequently, its insoluble fraction with $NaHCO_3$ aq. The resulting insoluble material was washed with water, dried and worked up by preparative TLC (adsorbent: Kieselgel G, Merck; development: benzene-cyclohexane 2:8). The fraction of the adsorbent containing the yellow main product was extracted with ether. The yellow crystalline product was shown by m.p. (232–4°), TLC and IR spectra to be identical with **20**.

When **18** was refluxed with xylene in the absence of P_2S_5, no change occurred, according to TLC, even after 2 hr.

Methyl N-(3-*phenyl*-2-*benzo*[b]*thienyl*)-*benzimidothioate* (**11**)

Metallic Na (0·3 g) and subsequently the thiobenzamide **10** (4·2 g; 12 mmoles) were dissolved in dry MeOH (30 ml), the soln was allowed to cool and MeI (1 ml) was added. Within a few min an orange oil started to precipitate. On the next morning the mother liquor was decanted from the oil which, when triturated with light petroleum, rapidly turned crystalline. 3·7 g (84%) **11**, faint yellow crystals, m.p. 108–110° (ethanol or gasoline).

The molecular formula, $C_{22}H_{17}NS_2$ was established by high resolution mass spectrometry,† IR (KBr): νC=N 1580; NMR ($CDCl_3$): ArH 470–430 Hz, m; S-Me 2·35 δ.

†Thanks are due for this determination to Dr. J. Møller, Copenhagen.

Methyl N-{6-*chloro*-3-(p-*chlorophenyl*)-2-*benzo*[b]-*thienyl*}-*benzimidothioate* (**21**)

This compound was obtained in 96% yield analogously to **11**, but starting with **20**, m.p.: 117–118° (gasoline).

The molecular formula, $C_{22}H_{15}Cl_2NS_2$ was established by high resolution mass spectrometry;† NMR ($CDCl_3$): ArH 460–435 Hz, m; S-Me 2·40δ.

N-*Benzylidene*-(3-*phenyl*-2-*benzo*[b]*thienyl*)-*amine* (**12**)

A mixture of **10** (2·0 g; 6 mmoles), Raney Ni (5·0 g) and dioxane (50 ml) was refluxed until (after about 10–15 hr) a TLC examination (adsorbent: Kieselgel G; development: benzene–cyclohexane 1 : 1) demonstrated the complete disappearance of the starting compound. The insoluble material was removed and washed with dioxane and the combined filtrate and washings were evaporated to dryness *in vacuo* to yield a red oily residue which, when triturated with light petroleum, turned crystalline. Recrystallization from EtOH gave 1·3 g (75%) of the fine faint yellow crystals of **12**, m.p.: 137–40° from EtOH. (Found: C, 80·78; H, 4·64; N, 4·54; S, 10·28. Calcd. for $C_{21}H_{15}NS$ (313·41): C, 80·47; H, 4·82; N, 4·47; S, 10·23%); NMR ($CDCl_3$): azomethine H 8·5 δ; ArH 475–420 Hz, m.

In the presence both of Na_2CO_3 or KOH the rate of the desulfuration diminished considerably. In the presence of KOH, for example, only the unchanged starting substance could be recovered even after 80 hr.

N-(3-*Phenyl*-2-*benzo*[b]*thienyl*)-*benzamide* (**13**)

(a) The thiobenzamide **10** (1·4 g; 4 mmoles) and SeO_2 (1·4 g; 12 mmoles) were refluxed in 90% aqueous dioxane (20 ml) for 2·5 hr. The selenium was filtered off and the filtrate diluted with water to yield 0·9 g of an orange crystalline product which was purified by preparative TLC (adsorbent: Kieselgel G; development: benzene; elution: $CHCl_3$) and recrystallization from aq MeOH. Creea coloured crystals, m.p.: 149–50°. (Found: C, 76·41; H, 4·50; N, 4·10; S, 9·69. Calcd. for $C_{21}H_{15}NOS$ (329·41): C, 76·56; H, 4·59; N, 4·25; S, 9·73%); IR (KBr): νNH 3415/3405 (d); Amide I 1670 cm^{-1}; NMR ($CDCl_3$): NH 8·8δ (b); ArH 480–435 Hz, m; UV (EtOH): 231 (4·50); 248 (4·24), sh; 308 (4·05).

(b) The same product was obtained by refluxing **10** and Hg(II) acetate (0·5 g, each) in AcOH (10 ml) for 8 hr, removing the black ppt (HgS) by filtration, diluting the filtrate with water and purifying the crude product by TLC as described under (a).

(c) The same product was also obtained by adding 30% H_2O_2 (5 ml) to a dioxane (25 ml) soln of **10** (1·7 g; 5 mmoles). The colour of the mixture turned dark red, heat was evolved and the soln started to boil spontaneously. After a few min the mixture was chilled in an ice bath, whereby its colour turned faint yellow. About 4 times its volume of water was added to the soln and the organic material was extracted with chloroform. The chloroform soln was washed with 5% $NaHCO_3$ aq and water, dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in chloroform (8 ml) and worked up by preparative TLC (4 plates; 20 × 20 cm, each; adsorbent: Kieselgel G, Merck; thickness of adsorbent layer 2 mm; development: benzene; detection: UV light; elution: EtOAc) to yield 0·5 g (31%) of **13**, faint yellow crystals, m.p. 149–150°. Identical according to their IR spectra with the product obtained according to (a).

(d) The same product was also obtained by SeO_2 (1·0 g) oxydation of **11** (0·6 g) in 90% aq dioxane (20 ml) (refluxing time about 4 hr) and working up the reaction mixture as described under (a).

Conversion of N-(3-*phenyl*-2-*benzo*[b]*thienyl*)-*benzamide* (**13**) *into the corresponding thiobenzamide* **10**.

A mixture of **13** (0·33 g; 1 mmole), P_2S_5 (0·22 g; 1 mmole) and dry dioxane (10 ml) was refluxed for 1·5 hr. The solvent was distilled off *in vacuo* and the residue was triturated with 5% $NaHCO_3$ aq to yield 0·30 g (87%) of pure yellow crystals of **10**, m.p. 190–192° (1-propanol), identified by IR spectrum and TLC (adsorbent: Kieselgel G, Merck; development: benzene–cyclohexane 1 : 1) with an authentic sample.

5-*Phenylbenzo*[4,5]*thieno*[2,3-c]*isoquinoline* (**14**)

Compound **10** (0·3 g; 1 mmole) was refluxed for 1 hr with anhyd $AlCl_3$ (0·3 g; 2·3 mmoles) in dry toluene (8 ml). The resulting mixture was poured into HCl aq and subsequently extracted with chloroform. The chloroform soln was washed, neutralized and dried as usual. The greater part of the solvent was evaporated and the soln was spotted onto a TLC plate, and chromatographed (adsorbent: Kieselgel G; development: benzene–cyclohexane, 6:4).‡ Finally the product was recrystallized from gasoline to yield the colourless crystals of **14**, m.p.: 185–6°.

The molecular formula, $C_{21}H_{13}NS$ was established by high resolution mass spectrometry.

3,9-*Dichloro*-5-*phenylbenzo*[4,5]*thieno*[2,3-c]*isoquinoline* (**15**).

(a) Compound **20** (0·4 g; 1 mmole) was refluxed for 1·5 hr with anhyd $AlCl_3$ (0·3 g; 2·3 mmoles) in dry toluene (8 ml). The resulting mixture was worked up as described above for **14** with the only difference that benzene was used as the solvent for extraction. The residue of evaporation of the benzene solvent was a yellow resinuous material which turned crystalline when triturated with light petroleum. The yield was 0·2 g (57%) of **15**, m.p. 228–9° from 1-propanol. (Found: Cl, 18·61; N, 3·90. Calcd. for $C_{21}H_{11}Cl_2NS$ (380·29): Cl, 18·65; N, 3·68%).

(b) The same product was obtained in the same yield by treating **21** similarly with $AlCl_3$.

Reaction of 5,5-*di*(p-*chlorophenyl*)-2-*phenyl*-2-*thiazoline*-2-*thione* (**18**) *with aluminium chloride*

A mixture of **18** (0·4 g; 1 mmole), anhyd $AlCl_3$ (0·3 g; 2·3 mmoles) and dry xylene (8 ml) was refluxed for 3 hr and subsequently poured into 20% HCl (30 ml). The mixture was extracted with EtOAc; the combined organic layers were neutralized by shaking with 5% $NaHCO_3$ aq, washed with water and evaporated to dryness *in vacuo*. The residue was dissolved in chloroform (8 ml) and worked up by chromatography on Kieselgel G, Merck (4 plates, 20 × 20 cm, each, thickness of adsorbent layer 2 mm; development: benzene-cyclohexane, 1:1; reference substances **15**, **18**, **20** and **22**, (see below); the spots corresponding to compounds **15** and **20** were eluted with ether and the residues obtained on evaporation of the solvent identified by comparison of their IR spectra with those of authentic samples.

The R_f values of **20** and **22** were identical in the system

†Thanks are due for this determination to Dr. J. Møller, Copenhagen.

‡Separation of the product from unchanged starting material could not be achieved by fractional crystallization.

used. As shown, however, by the fact that, according to its IR spectrum, compound **20** isolated by TLC was, even before recrystallization, almost pure, at best only traces of compound **22** were formed under the above conditions.

4,5-Bis(p-chlorophenyl)-2-phenylthiazole (**22**)

A mixture of *p,p'*-dichlorodesyl bromide† (0·9 g; 2·5 mmoles), thiobenzamide (0·4 g; 2·7 mmoles) and EtOH (10 ml) was refluxed for 2 hr. On cooling, the product was deposited partly in crystalline form and partly as a brownish oil which solidified slowly on standing. The crude product was recrystallized from EtOH to yield 0·8 g (80%) of **22**, colourless crystals, m.p. 126–128°. (Found: N, 3·88; S, 8·36. Calcd. for $C_{21}H_{13}Cl_2NS$ (382·29): N, 3·66; S, 8·39%).

Mass spectra were taken on a Varian MAT SM-1 mass spectrometer. The operating conditions were: resolution 1250; electron energy 70 eV; accelerating voltage 8 kV; source temperature 250°C. The following evaporation temperatures were used: **10** 130°; **11** 80°; **12** 110°; **13** 150°; and **14** 110°.

High resolution mass measurements were made at resolution 10,000 using PFT as the reference standard.

Crystal structure determination of N-(*-phenyl-2-benzo*[b]*-thienyl*)*-thiobenzamide* (**10**)

The orange crystals of the title compound show triclinic symmetry with the lattice parameters: a = 9·245 (13), b = 9·646 (12), c = 10·799 (18) Å, $\alpha = 111·9(1)°$, $\beta = 88·9(1)°$ and $\gamma = 104·6(2)°$, V = 862·16 Å,^{3} determined from precession photographs and checked by diffractometer. $D_c = 1·331$, $D_x = 1·337$ g cm^{-3} (by flotation) Z = 2, sp. gr. Pl. 2257 independent reflexions were collected from crystal layers of 0kl → 7kl on a Stoe semi-automatic two-circle diffractometer, 247 of them were unobserved. The crystal structure was solved by the symbolic addition method using a program written by Germain, Main and Woolfson.[24] The E-map computed from 376 reflexions ($E_H \geq 1·40$) showed two molecules in the asymmetric unit overlapping each other. This striking result[25] is probably due to rational dependence of the atomic coordinates causing a non-uniform distribution of $\langle|E_H|\rangle^2$ throughout the reciprocal space.[26] From the numerous peaks one thionaphtene and two visibly parallel phenyl groups were clearly resolved, however. Further study of the E-map and the packing possibilities of the molecular fragments found, along with the chemical evidence, resulted in the location of the thiobenzamide group and excluded the phenyl ring seemingly connected to the N atom as a real part of the molecule revealed. Structure factor calculation using fractional atomic coordinates derived from the E-map and an overall temperature factor of 3·0 Å^2 gave an R value of 0·51 which was reduced to 0·39 when the molecule supposed to be correct was shifted in the unit cell by the half distance of the parallel phenyl rings (*i.e.* by $\Delta x = -0·020$, $\Delta y = 0·145$, $\Delta z = 0·105$). Next structure factor calculation with coordinates improved from a Fourier synthesis yielded an R of 0·269. Refinement with isotropic and anisotropic temp factors reduced the residual to 0·076. Eleven H atoms were clearly visible in a difference map computed at this stage. The other four smeared strongly were located with the help of hydrogen positions generated. Further anisotropic refinement in which the H atoms were included in isotropic mode resulted in the final R factor of 0·050 for observed reflexions, when the shifts in coordinates were less than $0·3\sigma_{av}$. Inclusion of 13 reflexions affected by extinction and the unobserved one gave an R value of 0·071. All calculations were performed on a CDC 3300 computer using atomic scattering factors for all atoms given in the International Tables for X-ray Crystallography.[27]

†Prepared from the corresponding deoxybenzoin[23] by bromination with N-bromosuccinimide in tetrachloromethane.

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