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An Unexpected Synthesis of Thiophene Derivatives by Thionation of *N*-Phenylacetylthiobenzamides*

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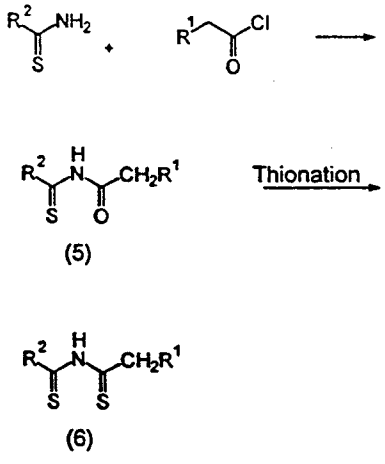
ABSTRACT

Four thiophene derivatives have been obtained unexpectedly from the reaction of N-phenylacetylthiobenzamides with P_4S_{10} in boiling carbon disulfide. The structure of one of these was established by X-ray crystallography.

INTRODUCTION

In continuation of our work on the synthesis of various types of 1,6,6aλ^4 triheterapentalenes, we have attempted to prepare novel and versatile starting materials of structure (**1**). The heterocyclic moiety of compounds (**1**) is similar to that of (**2**) except that the carbon atom at position 4 is replaced by a nitrogen atom. Compounds of general structure (**2**) were found to be versatile starting materials for the synthesis of 1,6,6aλ^4 triheterapentalenes (**3**) [1–3] and their 2-aza analogues (**4**) [4,5]. We considered the possibility of preparing a precursor of the dithiazolium salts (**1**) according to Scheme 1. It was our expectation that thionation of the *N*-acylthiobenzamides (**5**) [6,7] would lead to the *N*-thioacylthiobenzamides (**6**) which, when oxidized with bromine, would produce the dithiazolium salts (**1**). However, when the *N*-acylthiobenzamides (**5**) were allowed to react with P_4S_{10}, compounds (**6**) were not isolated. This article re-



(5a) - (7a) : R^1 = Ph R^2 = Ph
(5b) - (7b) : R^1 = *p*-Methoxyphenyl R^2 = Ph
(5c) - (7c) : R^1 = Ph R^2 = *p*-Tolyl
(5d) - (7d) : R^1 = *p*-Methoxyphenyl R^2 = *p*-Tolyl
(5e) : R^1 = Me R^2 = Ph

SCHEME 1

*Studies of Heterocyclic Compounds, Part 33.
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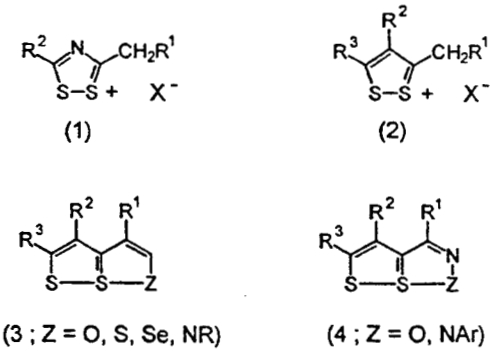
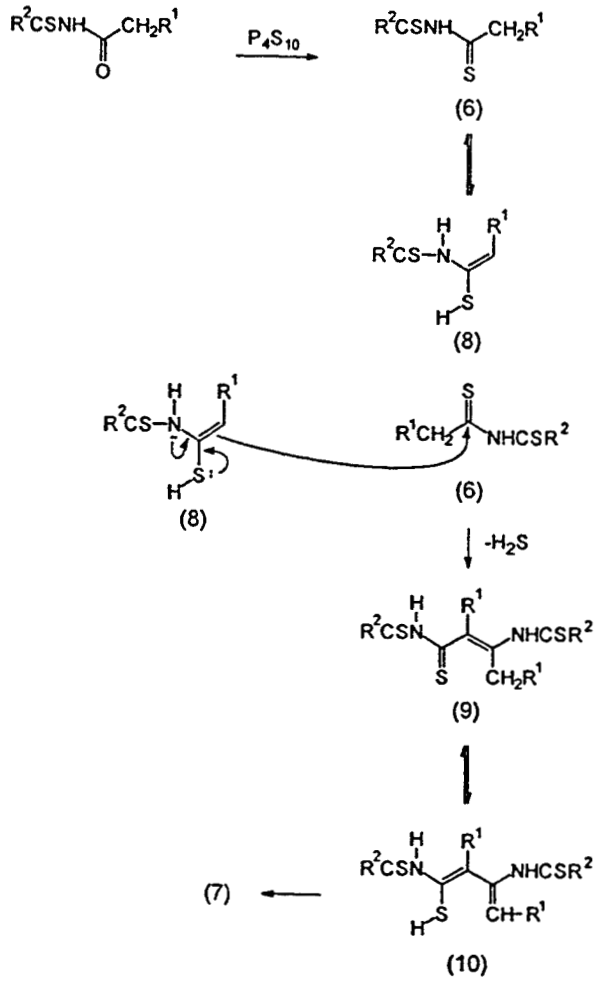
ports the results of studies of the thionation of the *N*-acylthiobenzamides (**5**).



RESULTS AND DISCUSSION

The *N*-acylthiobenzamides (**5a**)–(**5e**) were prepared by reaction of the appropriate thiobenzamides with acylchlorides [6,7]. However, thionation of compounds (**5a**)–(**5d**) with P_4S_{10} in boiling carbon disulfide did not give the desired products (**6**) but unexpectedly led to thiophene derivatives of structure (**7**). When compound (**5a**) was treated with Lawesson's reagent [8] or P_4S_{10} in boiling benzene, and compound (**5b**) was allowed to react with a mixture of P_4S_{10}-Na_2CO_3 (1 : 1) [9] in boiling THF, the same products (**7a**) and (**7b**) were obtained but in a lower yield. It is still not clear how the thiophene derivatives were formed, but one possible pathway is suggested in Scheme 2. The first step in the course of the reaction may involve the formation of the intermediate (**6**), which equilibrates with the enamine-vinyl thioether (**8**). Condensation of (**8**) with its tautomer (**6**) gives (**9**) or its tautomer (**10**). Under our reaction conditions, intermediate (**9**) or (**10**) would then be dehydrogenated by P_4S_{10} or sulfur therefrom or be oxidized by air and produce the final thiophene product (**7**). Compound (**5e**) was also treated with P_4S_{10} under the same reaction conditions, but no thiophene derivative was isolated. It is likely that the reaction pathway in Scheme 2 is specific for the *N*-phenylacetylthioamides in which the high acidity of the benzyl protons is the major factor that leads to the formation of intermediates (**6**) ⇌ (**8**) and finally to the thiophene. Cyclic dithioimides (**11**) and (**12**) have been prepared by reaction of the corresponding imides with Lawesson's reagent [8], but under more vigorous reaction conditions. Compound (**7d**), representing this series of products, was studied by X-ray crystallography (Figure 1). Selected bond lengths and bond angles are given in Tables 1 and 2, respectively. The lengths of the C–N and C=S bonds in the thioamide moieties (C19–N2, 1.351(6) Å; C19=S3, 1.657(5) Å; C27–N1, 1.346(6) Å; C27=S2, 1.671(4) Å;) fall in the range found for thioamides (C–N, 1.35 Å; C=S, 1.66 Å; [10]). Bond lengths and bond angles in the thiophene ring in (**7d**) are unex-



SCHEME 2

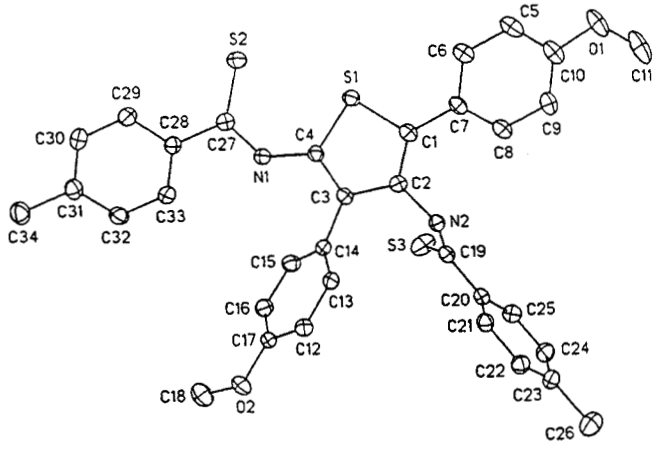
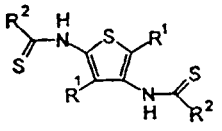


FIGURE 1 ORTEP drawing of one molecule of the thiophene derivative (**7d**). Hydrogen atoms are omitted for clarity.

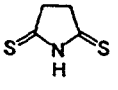
TABLE 1 Thiophene Derivative **7d**: Selected Bond Lengths

Atom 1	*Atom 2*	*Length (Å)*	*Atom 1*	*Atom 2*	*Length (Å)*
S1	C1	1.745(4)	S1	C4	1.738(4)
S2	C27	1.671(4)	S3	C19	1.657(5)
N1	C4	1.398(5)	N1	C27	1.346(6)
N2	C2	1.429(5)	N2	C19	1.351(6)
C1	C2	1.375(5)	C1	C7	1.483(5)
C2	C3	1.426(5)	C3	C4	1.364(6)
C3	C14	1.482(5)	—	—	—

ceptional. The lengths of the carbon–carbon and carbon–sulfur bonds in the thiophene ring of (**7d**) are similar to those of corresponding bonds in thiophene itself (C2–C3, 1.362 Å; C3–C4, 1.424 Å; C–S, 1.712 Å; [10]).



(7)



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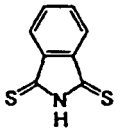

(12)

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus. ^{1}H NMR spectra were determined at 200.13 MHz and ^{13}C NMR spectra at 50.32 MHz with a Bruker AC spectrometer. ^{1}H NMR chemical shifts are given in parts per million downfield from tetramethylsilane as internal reference. Unless otherwise stated, δ values refer to singlet absorptions. Data are given in the following order: δ value, number of protons, multiplicity (d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), J(Hz), and assignment. ^{1}H NMR signals assigned to the pairs of *o*- and *m*-protons of the *p*-substituted phenyl group in compounds (**5b**) and (**5d**) are the four most intense signals in the AA'BB' pattern. ^{13}C NMR chemical shifts are given relative to the central deuteriochloroform peak taken as δ 77.00 and are proton-decoupled values.

TABLE 2 Thiophene Derivative **7d**: Selected Bond Angles

Atom 1	*Atom 2*	*Atom 3*	*Angle (°)*	*Atom 1*	*Atom 2*	*Atom 3*	*Angle (°)*
C1	S1	C4	91.2(2)	C4	N1	C27	133.8(3)
S1	C1	C7	119.6(3)	S1	C1	C2	110.3(3)
N2	C2	C1	124.7(3)	C2	C1	C7	130.2(4)
C1	C2	C3	114.5(4)	N2	C2	C3	120.8(3)
C2	C3	C14	125.8(4)	C2	C3	C4	111.1(3)
S1	C4	N1	126.0(3)	C4	C3	C14	122.9(3)
N1	C4	C3	120.8(3)	S1	C4	C3	112.9(3)

Extracts were dried over sodium sulfate. Solvents were removed from extracts and chromatographic eluates at reduced pressure with a rotary evaporator. Acetonitrile, benzene, carbon disulfide, dichloromethane, DMF (dimethylformamide), hexane, THF (tetrahydrofuran), and pyridine were dried by standard procedures and redistilled before use. Phenylacetyl chloride, propionyl chloride, and thiobenzamide were commercially available materials. *p*-Methoxyphenylacetyl chloride [11] and *p*-methylthiobenzamide [12] were prepared according to the references cited. Column chromatography was carried out with silica (70–200 mesh).

General Procedure for the Preparation of the N-Acylthioamides (**5a**)–(**5e**)

The thiobenzamide was dissolved in dry acetonitrile and 1 equivalent of the acyl chloride followed by dry pyridine (0.1 mL/mmol) was then added. The resulting solution was heated under reflux for 15 minutes with exclusion of moisture, then poured into water. The resulting mixture was extracted successively with benzene and dichloromethane. The dichloromethane extract was discarded if it did not contain any reaction product. The combined organic extracts were washed with 2M-aqueous HCl, then dried and evaporated at reduced pressure. The residue was recrystallized from dichloromethane-hexane (1:3). The following *N*-acylthiobenzamides were thus prepared and used for reaction without further purification.

N-Phenylacetylthiobenzamide (**5a**). This compound (11.0 g, 86%) was obtained from thiobenzamide (6.85 g, 50.0 mmol) and phenylacetyl chloride (6.60 mL, 50.0 mmol) in acetonitrile (50 mL). A sample for identification was chromatographed (5 × 2.0 cm, CH_2Cl_2), then recrystallized from ethanol-water (1:1), and obtained as orange plates, mp 114–115°C (Ref. [6]: 114–115°C).

N-(p-Methoxyphenylacetyl)thiobenzamide (**5b**). This compound (12.3 g, 86%) was obtained from thiobenzamide (6.85 g, 50.0 mmol) and *p*-methoxyphenylacetyl chloride (7.65 mL, 50.0 mmol) in acetonitrile (50 mL). A sample for characterization

TABLE 3 Summary of Crystal Data and Intensity Collection 92JN04 (920105)

Empirical formula	$C_{34}H_{30}N_2O_2S_3$
Color; habit	orange; chunk
Crystal size (mm)	0.48 × 0.44 × 0.38
Space group	$P2_1/c$; monoclinic
Unit cell dimensions	a = 11.351(3) Å
	b = 20.804(7) Å; β = 111.68(2)°
	c = 14.162(5) Å
No. reflections for indexing	15 (11.73° ≤ 2θ ≤ 25.30°)
Volume	3107.7(16) Å^3
Z	4
Formula weight	594.8
Density (calcd)	1.271 Mg/m^3
Absorption coefficient	0.260 mm^{-1}
F(000)	1248
Diffractometer used	Siemens R3m/V
Radiation	Mo K_α (λ = 0.71073 Å)
Temperature (K)	296
2θ range	2.5 to 50.0°
Scan type	$\theta/2\theta$
Scan speed	variable; 2.93 to 14.65°/min in ω
Scan range (ω)	1.00° plus K_α separation
Background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	three measured every 50 reflections
Index ranges	$-13 \leq h \leq 12.0 \leq k \leq 24.0 \leq l \leq 16$
Reflections collected	5984 (3004 ≥ 3.0σ(I))
Independent reflections	5508 (2759 ≥ 3.0σ(I)) (R_{int} = 16.92%)
Extinction correction	χ = 0.00023(10), where $F^* = F\,[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Number of parameters refined	371
Final R indices (obsd data)	R = 0.0450, R_w = 0.0473
Goodness-of-fit	1.33
Largest and mean Δ/σ	0.001, 0.000
Data-to-parameter ratio	7.4:1
Largest difference peak/hole	0.20/−0.23 e Å^{-3}

was chromatographed (5 × 2.0 cm, CH_2Cl_2), then recrystallized from benzene, and obtained as reddish-orange plates, mp 99–100°C; ^{1}H NMR ($CDCl_3$) δ 3.78 (3H, s, OMe), 3.82 (2H, s, CH_2), 6.87 and 6.92 (2H, 2 *o*-protons of C_6H_4), 7.17 and 7.21 (2H, 2 *m*-protons of C_6H_4), 7.24–7.53 (5H, m, Ph), 9.74 (1H, s, NH); ^{13}C NMR ($CDCl_3$) δ 43.67 (CH_2), 55.17 (OMe), 114.41, 124.78, 127.11, 128.07, 130.53, 131.74, 141.94 and 159.01 (C of Ph and C_6H_4), 169.88 (C=0), 203.35 (C=S). Anal. calcd for $C_{16}H_{15}NO_2S$: C, 67.34; H, 5.30; N, 4.90. Found: C, 67.44; H, 5.22; N, 4.91%.

N-Phenylacetyl-p-methylthiobenzamide (**5c**). This compound (5.41 g, 81%) was obtained from *p*-methylthiobenzamide (3.77 g, 25.0 mmol) and phenylacetyl chloride (3.30 mL, 25.0 mmol) in acetonitrile (25 mL). A sample for identification was chromatographed (5 × 2.0 cm, CH_2Cl_2), then recrystallized from dichloromethane-acetonitrile (1:4), and obtained as orange plates, mp 145–147°C (Ref. [6]: 147°C).

N-(p-Methoxyphenylacetyl)-p-methylthiobenzamide (**5d**). This compound (6.26 g, 84%) was obtained from *p*-methylthiobenzamide (3.77 g, 25.0 mmol) and *p*-methoxyphenylacetyl chloride (3.83 mL, 25.0 mmol) in acetonitrile (25 mL). A sample for microanalysis was chromatographed (5 × 2.0 cm, CH_2Cl_2), then recrystallized from dichloromethane-acetonitrile (1:4), and obtained as red plates, mp 118–120°C; ^{1}H NMR ($CDCl_3$) δ 2.32 (3H, s, OMe), 3.79 (3H, s, O-Me), 3.85 (2H, s, CH_2), 6.87 and 6.92 (2H, 2 *o*-protons of *p*-tolyl), 7.07 and 7.11 (2H, 2 *o*-protons of $MeOC_6H_4$), 7.18 and 7.23 (2H, 2 *m*-protons of *p*-tolyl), 7.43 and 7.47 (2H, 2 *m*-protons of $MeOC_6H_4$), 9.66 (1H, s, NH); ^{13}C NMR ($CDCl_3$) δ 21.45 (Me), 43.83 (CH_2), 55.24 (OMe), 114,50, 124.95, 127.39, 128.85, 130.63, 139.32, 143.01 and 159.09 (C of 2 C_6H_4), 169.97 (C=O), 202.94 (C=S). Anal. calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.36; H, 5.72; N, 4.66%.

N-Propionylthiobenzamide (**5c**). This compound (7.57 g, 73%) was obtained from thioben-

TABLE 4 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U(eq)*[a]
S(1)	37(1)	−40(1)	3537(1)	51(1)
S(2)	2066(1)	−1184(1)	4140(1)	64(1)
S(3)	835(1)	2277(1)	3265(1)	82(1)
N(1)	2460(3)	−49(2)	5059(2)	50(1)
N(2)	−480(3)	1752(2)	4255(2)	44(1)
O(1)	−5830(3)	811(2)	575(3)	102(2)
O(2)	4955(3)	2020(2)	8110(3)	96(2)
C(1)	−805(4)	675(2)	3439(3)	48(2)
C(2)	−69(4)	1121(2)	4119(3)	44(2)
C(3)	1174(3)	903(2)	4720(3)	43(2)
C(4)	1354(3)	283(2)	4492(3)	45(2)
C(5)	−4111(5)	230(3)	1658(4)	75(2)
C(6)	−2887(4)	184(2)	2361(3)	60(2)
C(7)	−2119(4)	726(2)	2685(3)	49(2)
C(8)	−2631(4)	1314(2)	2260(3)	59(2)
C(9)	−3864(4)	1361(3)	1549(3)	67(2)
C(10)	−4612(4)	816(3)	1251(3)	73(2)
C(11)	−6383(5)	1396(4)	125(4)	126(4)
C(12)	2849(4)	1754(2)	7215(3)	58(2)
C(13)	1891(4)	1497(2)	6391(3)	48(2)
C(14)	2134(3)	1269(2)	5547(3)	43(2)
C(15)	3348(4)	1351(2)	5550(3)	56(2)
C(16)	4319(4)	1608(2)	6385(4)	62(2)
C(17)	4069(4)	1795(2)	7223(4)	61(2)
C(18)	6225(5)	1984(3)	8238(5)	136(4)
C(19)	−51(4)	2295(2)	3969(3)	48(2)
C(20)	−438(3)	2907(2)	4308(3)	43(2)
C(21)	−628(4)	2956(2)	5227(3)	48(2)
C(22)	−993(4)	3531(2)	5512(3)	54(2)
C(23)	−1206(4)	4074(2)	4913(4)	59(2)
C(24)	−1009(4)	4031(2)	4001(3)	61(2)
C(25)	−613(4)	3461(2)	3712(3)	55(2)
C(26)	−1651(5)	4698(3)	5223(4)	87(3)
C(27)	2903(4)	−641(2)	4995(3)	49(2)
C(28)	4209(4)	−753(2)	5752(3)	46(2)
C(29)	4640(4)	−1368(2)	6090(3)	57(2)
C(30)	5838(5)	−1463(2)	6804(3)	64(2)
C(31)	6667(4)	−958(3)	7207(3)	60(2)
C(32)	6257(4)	−347(2)	6857(3)	63(2)
C(33)	5050(4)	−241(2)	6145(3)	60(2)
C(34)	7978(4)	−1064(3)	7989(4)	82(2)

[a]Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5 Bond Lengths (Å)

S(1)–C(1)	1.745(4)	S(1)–C(4)	1.738(4)
S(2)–C(27)	1.671(4)	S(3)–C(19)	1.657(5)
N(1)–C(4)	1.398(5)	N(1)–C(27)	1.346(6)
N(2)–C(2)	1.429(5)	N(2)–C(19)	1.351(6)
O(1)–C(10)	1.361(5)	O(1)–C(11)	1.410(8)
O(2)–C(17)	1.370(5)	O(2)–C(18)	1.387(7)
C(1)–C(2)	1.375(5)	C(1)–C(7)	1.483(5)
C(2)–C(3)	1.426(5)	C(3)–C(4)	1.364(6)
C(3)–C(14)	1.482(5)	C(5)–C(6)	1.382(6)
C(5)–C(10)	1.377(8)	C(6)–C(7)	1.395(6)
C(7)–C(8)	1.391(6)	C(8)–C(9)	1.393(5)
C(9)–C(10)	1.387(8)	C(12)–C(13)	1.376(5)
C(12)–C(17)	1.384(7)	C(13)–C(14)	1.405(7)
C(14)–C(15)	1.387(6)	C(15)–C(16)	1.391(6)
C(16)–C(17)	1.374(8)	C(19)–C(20)	1.482(6)
C(20)–C(21)	1.400(6)	C(20)–C(25)	1.399(6)
C(21)–C(22)	1.375(6)	C(22)–C(23)	1.379(6)
C(23)–C(24)	1.393(8)	C(23)–C(26)	1.515(7)
C(24)–C(25)	1.382(7)	C(27)–C(28)	1.492(5)
C(28)–C(29)	1.390(6)	C(28)–C(33)	1.400(6)
C(29)–C(30)	1.376(6)	C(30)–C(31)	1.385(7)
C(31)–C(32)	1.381(7)	C(31)–C(34)	1.507(6)
C(32)–C(33)	1.387(5)	—	—

TABLE 6 Bond Angles (°)

C(1)–S(1)–C(4)	91.2(2)	C(4)–N(1)–C(27)	133.8(3)
C(2)–N(2)–C(19)	123.8(4)	C(10)–O(1)–C(11)	118.6(5)
C(17)–O(2)–C(18)	118.5(5)	S(1)–C(1)–C(2)	110.3(3)
S(1)–C(1)–C(7)	119.6(3)	C(2)–C(1)–C(7)	130.2(4)
N(2)–C(2)–C(1)	124.7(3)	N(2)–C(2)–C(3)	120.8(3)
C(1)–C(2)–C(3)	114.5(4)	C(2)–C(3)–C(4)	111.1(3)
C(2)–C(3)–C(14)	125.8(4)	C(4)–C(3)–C(14)	122.9(3)
S(1)–C(4)–N(1)	126.0(3)	S(1)–C(4)–C(3)	112.9(3)
N(1)–C(4)–C(3)	120.8(3)	C(6)–C(5)–C(10)	120.8(5)
C(5)–C(6)–C(7)	121.4(4)	C(1)–C(7)–C(6)	121.2(4)
C(1)–C(7)–C(8)	121.6(4)	C(6)–C(7)–C(8)	117.2(3)
C(7)–C(8)–C(9)	121.5(4)	C(8)–C(9)–C(10)	120.0(5)
O(1)–C(10)–C(5)	116.3(5)	O(1)–C(10)–C(9)	124.7(5)
C(5)–C(10)–C(9)	119.1(4)	C(13)–C(12)–C(17)	120.3(5)
C(12)–C(13)–C(14)	120.7(4)	C(3)–C(14)–C(13)	121.8(4)
C(3)–C(14)–C(15)	120.3(4)	C(13)–C(14)–C(15)	117.6(3)
C(14)–C(15)–C(16)	121.6(5)	C(15)–C(16)–C(17)	119.4(5)
O(2)–C(17)–C(12)	114.9(5)	O(2)–C(17)–C(16)	125.0(4)
C(12)–C(17)–C(16)	120.1(4)	S(3)–C(19)–N(2)	121.8(3)
S(3)–C(19)–C(20)	122.2(3)	N(2)–C(19)–C(20)	116.0(4)
C(19)–C(20)–C(21)	122.0(4)	C(19)–C(20)–C(25)	120.3(4)
C(21)–C(20)–C(25)	117.6(4)	C(20)–C(21)–C(22)	120.2(4)
C(21)–C(22)–C(23)	122.4(5)	C(22)–C(23)–C(24)	117.7(4)
C(22)–C(23)–C(26)	121.6(5)	C(24)–C(23)–C(26)	120.6(4)
C(23)–C(24)–C(25)	120.7(4)	C(20)–C(25)–C(24)	121.2(5)
S(2)–C(27)–N(1)	122.7(3)	S(2)–C(27)–C(28)	124.3(3)
N(1)–C(27)–C(28)	113.0(3)	C(27)–C(28)–C(29)	121.3(4)
C(27)–C(28)–C(33)	121.2(4)	C(29)–C(28)–C(33)	117.5(3)
C(28)–C(29)–C(30)	120.8(4)	C(29)–C(30)–C(31)	122.0(4)
C(30)–C(31)–C(32)	117.5(4)	C(30)–C(31)–C(34)	121.9(4)
C(32)–C(31)–C(34)	120.5(4)	C(31)–C(32)–C(33)	121.3(4)
C(28)–C(33)–C(32)	120.9(4)	—	—

zamide (6.85 g, 50.0 mmol) and propionyl chloride (4.34 mL, 50.0 mmol) in acetonitrile (50 mL). A sample for identification was chromatographed (5 × 2.0 cm, CH_2Cl_2), then recrystallized from CH_2Cl_2-hexane (1:5), and obtained as red plates, mp 90–91°C (Ref. [6]: 91°C).

General Procedure for the Preparation of the Thiophenes (**7a**)–(**7d**)

The *N*-acylthiobenzamide (5 mmol) and P_4S_{10} (2.20 g, 5 mmol) were added to dry carbon disulfide (50 mL), and the resulting mixture was heated under

TABLE 7 Anisotropic Displacement Coefficients ($A^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	49(1)	52(1)	49(1)	−5(1)	15(1)	−7(1)
S(2)	64(1)	57(1)	67(1)	−4(1)	19(1)	−14(1)
S(3)	109(1)	68(1)	102(1)	−2(1)	79(1)	−1(1)
N(1)	47(2)	48(2)	51(2)	0(2)	14(2)	−7(2)
N(2)	39(2)	48(2)	46(2)	0(2)	16(2)	1(2)
O(1)	49(2)	152(4)	75(3)	−11(2)	−11(2)	9(3)
O(2)	54(2)	93(3)	103(3)	6(2)	−16(2)	−38(2)
C(1)	44(2)	57(3)	45(2)	−5(2)	19(2)	0(2)
C(2)	44(3)	46(3)	47(2)	−3(2)	23(2)	1(2)
C(3)	38(2)	52(3)	40(2)	−3(2)	16(2)	−1(2)
C(4)	39(2)	49(3)	48(2)	0(2)	16(2)	−4(2)
C(5)	57(3)	93(4)	65(3)	−26(3)	12(3)	−6(3)
C(6)	54(3)	71(3)	52(3)	−12(2)	16(2)	−3(2)
C(7)	42(2)	66(3)	40(2)	−7(2)	15(2)	−2(2)
C(8)	50(3)	75(3)	46(3)	−8(3)	13(2)	−4(2)
C(9)	51(3)	89(4)	55(3)	6(3)	13(2)	9(3)
C(10)	49(3)	111(5)	54(3)	−12(3)	13(3)	1(3)
C(11)	56(4)	209(8)	86(4)	−1(4)	−6(3)	41(5)
C(12)	59(3)	56(3)	51(3)	8(2)	12(2)	−11(2)
C(13)	44(2)	49(3)	49(3)	5(2)	15(2)	−4(2)
C(14)	41(2)	38(2)	48(2)	1(2)	14(2)	0(2)
C(15)	46(3)	57(3)	68(3)	−8(2)	26(2)	−11(2)
C(16)	41(3)	57(3)	89(4)	−2(2)	25(3)	−14(3)
C(17)	42(3)	46(3)	74(3)	5(2)	−3(2)	−13(2)
C(18)	61(4)	124(6)	167(7)	7(4)	−24(4)	−45(5)
C(19)	44(2)	57(3)	40(2)	−2(2)	13(2)	0(2)
C(20)	35(2)	50(3)	42(2)	0(2)	11(2)	1(2)
C(21)	47(2)	53(3)	41(2)	4(2)	13(2)	4(2)
C(22)	56(3)	60(3)	50(3)	5(2)	23(2)	−3(2)
C(23)	53(3)	53(3)	69(3)	6(2)	23(2)	−4(3)
C(24)	66(3)	53(3)	64(3)	2(2)	22(3)	9(2)
C(25)	60(3)	56(3)	50(3)	−4(2)	22(2)	3(2)
C(26)	93(4)	73(4)	110(4)	6(3)	56(4)	−2(3)
C(27)	51(3)	52(3)	50(3)	−2(2)	26(2)	−1(2)
C(28)	46(2)	50(3)	46(2)	4(2)	20(2)	1(2)
C(29)	58(3)	51(3)	64(3)	1(2)	25(2)	1(2)
C(30)	63(3)	59(3)	68(3)	16(3)	22(3)	11(3)
C(31)	54(3)	73(4)	55(3)	13(3)	22(2)	−2(3)
C(32)	51(3)	66(3)	67(3)	−2(3)	17(3)	−12(3)
C(33)	54(3)	51(3)	70(3)	6(2)	17(3)	−3(2)
C(34)	68(3)	95(4)	73(3)	28(3)	14(3)	−6(3)

The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

TABLE 8 H-Atom Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	U
H(1A)	2989	183	5579	80
H(2A)	−1059	1788	4547	80
H(5A)	−4622	−150	1450	80
H(6A)	−2556	−230	2630	80
H(8A)	−2126	1695	2471	80
H(9A)	−4190	1772	1262	80
H(11A)	−7242	1334	−333	80
H(11B)	−6366	1698	643	80
H(11C)	−5889	1561	−244	80
H(12A)	2670	1901	7791	80
H(13A)	1044	1476	6388	80
H(15A)	3520	1232	4958	80
H(16A)	5158	1653	6379	80
H(18A)	6762	2149	8888	80
H(18B)	6469	1550	8164	80
H(18C)	6311	2246	7709	80
H(21A)	−503	2588	5663	80
H(22A)	−1108	3557	6150	80
H(24A)	−1152	4401	3568	80
H(25A)	−459	3445	3090	80
H(26A)	−1734	4646	5869	80
H(26B)	−1044	5030	5272	80
H(26C)	−2456	4814	4720	80
H(29A)	4103	−1732	5819	80
H(30A)	6104	−1891	7042	80
H(32A)	6822	11	7105	80
H(33A)	4787	189	5920	80
H(34D)	8116	−1511	8158	80
H(34A)	8586	−918	7712	80
H(34B)	8073	−821	8589	80

reflux for 1.5 hours, then poured into saturated aqueous sodium carbonate (30 mL). The resulting solution was extracted with dichloromethane (250 mL × 3), and the combined extracts were dried and then evaporated at reduced pressure. The residue was recrystallized from benzene to yield the thiophene. Samples for microanalysis were purified by chromatography (CH_2Cl_2), followed by recrystallization. As so many aromatic carbons are present in the reaction products (**7a**)–(**7d**), not all the ^{13}C signals were detected; some of them overlap in the range of δ = 120–160.

2,4-Diphenyl-3,5-di-(N-thiobenzamido)thiophene (**7a**). Compound (**7a**) (0.62 g, 49%) was obtained from *N*-phenylacetylthiobenzamide (1.28 g). A sample for microanalysis was recrystallized from DMF-benzene (1:9) and obtained as yellow needles, mp 267–269°C; ^1H NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 7.29–7.55 (20H, m, protons of 4 Ph), 11.31 (1H, s, NH), 11.35 (1H, s, NH); ^{13}C NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 125.89, 125.99, 126.54, 126.67, 126.80, 127.08, 127.41, 128.05, 129.11, 129.35, 129.70, 130.32, 131.18, 131.41, 131.83, 134.18, 139.91 and 139.98 (C of 4 Ph and thiophene), 194.44 (C = S), 199.81 (C=S). Anal. calcd for $C_{30}H_{22}N_2S_3$: C, 71.12; H, 4.37; N, 5.53. Found: C, 71.33; H, 4.29; N, 5.48%.

2,4-Di-(p-methoxyphenyl)-3,5-di-(N-thiobenzamido)thiophene (**7b**). Compound (**7b**) (0.52 g, 37%) was obtained from *N*-*p*-methoxyphenylacetylthiobenzamide (1.33 g). A sample for microanalysis was recrystallized from dichloromethane-benzene (1:2) and obtained as yellow needles, mp 272–274°C; ^1H NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 3.76 (3H, s, OMe), 3.78 (3H, s, OMe), 6.89–6.96 + 7.28–7.76 (18H, m, protons of 2 Ph and 2 C_6H_4), 11.08 (1H, s, NH), 11.24 (1H, s, NH); ^{13}C NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 53.79 (OMe), 53.89 (OMe), 112.58,

112.87, 123.64, 124.03, 126.00, 126.62, 126.89, 127.99, 128.54, 129.29, 129.43, 129.72, 130.33, 131.14, 133.08, 139.96, 139.99, 157.83 and 158.08 (C of 2 Ph, 2 C_6H_4 and thiophene), 193.82 (C=S), 199.82 (C=S). Anal. calcd for $C_{32}H_{26}N_2O_2S_3$: C, 67.82; H, 4.62; N, 4.94. Found: C, 67.50; H, 4.50; N, 4.82%.

2,4-Diphenyl-3,5-di-(N-p-methylthiobenzamido)-thiophene (**7c**). Compound (**7c**) (0.90 g, 68%) was obtained from *N*-phenylacetyl-*p*-methylthiobenzamide (1.35 g). A sample for microanalysis was recrystallized from benzene and obtained as yellow plates, mp 260–262°C. Based on the microanalysis data, these crystals contained 0.25 equivalent of benzene. ^{1}H NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 2.34 (3H, s, Me), 2.36 (3H, s, Me), 7.21–7.75 (18H, m, protons of 2 Ph and 2 C_6H_4), 11.49 (1H, s, NH), 11.72 (1H, s, NH); ^{13}C NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 20.73 (Me), 20.76 (Me), 127.06, 127.48, 127.52, 128.01, 128.17, 128.40, 128.49, 128.80, 128.91, 130.53, 132.14, 132.44, 133.00, 133.89, 135.04, 137.71, 138.01, 141.02 and 141.35 (C of 2 Ph, 2 C_6H_4 and thiophene), 197.21 (C=S), 199.80 (C=S). Anal. calcd for $C_{32}H_{26}N_2S_3 + (1/4)C_6H_6$: C, 73.27; H, 5.09; N, 4.88. Found: C, 73.38; H, 5.00; N, 4.87%.

2,4-Di-(p-methoxyphenyl)-3,5-di-(N-p-methylthiobenzamido)thiophene (**7d**). Compound (**7d**) (1.10 g, 74%) was obtained from *N*-*p*-methoxyphenylacetyl-*p*-methylthiobenzamide (1.50 g). A sample for microanalysis was recrystallized from benzene and obtained as yellow needles, mp 219–222°C; ^{1}H NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 2.34 (3H, s, Me), 2.35 (3H, s, Me), 6.86–7.66 (16H, m, protons of 4 C_6H_4), 10.63 (1H, s, NH), 11.52 (1H, s, NH); ^{13}C NMR [$CDCl_3$ + DMSO-D_6 (1:3)] δ 20.24 (2Me), 54.08 (OMe), 54.16 (OMe), 113.13, 123.99, 124.05, 126.02, 126.42, 127.22, 127.51, 127.97, 128.29, 128.84, 129.59, 129.93, 130.65, 133.41, 137.29, 137.38, 140.18, 140.70, 158.22 and 158.32 (C of 4 C_6H_4 and thiophene), 192.41 (C=S), 199.97 (C=S). Anal. calcd for $C_{34}H_{30}N_2O_2S_3$: C, 68.66; H, 5.08; N, 4.71. Found: C, 68.80; H, 5.03; N, 4.66%.

Additional Thionation Reactions of Compounds (**5a**) *and* (**5b**)

(a) Reaction of *N*-phenylacetylthiobenzamide (**5a**) (1.28 g, 5 mmol) with an excess of P_4S_{10} (2.2 g, 5 mmol) in boiling benzene for 1 hour or with Lawesson's reagent (1.01 g, 2.5 mmol) in boiling benzene for 6 hours gave 2,4-diphenyl-3,5-di-(*N*-thiobenzamido)thiophene (**7a**) in 40% and 18% yields, respectively, mp and mixed mp with an authentic sample 267–269°C.

(b) 2,4-Di-(*p*-methoxyphenyl)-3,5-di-(*N*-thiobenzamido)thiophene (**7b**) (0.34 g, 24.1%) was also obtained from the reaction of *N*-*p*-methoxyphenylacetylthiobenzamide (**5b**) (1.33 g, 5 mmol) with a 1:1 mixture of Na_2CO_3 (0.53 g)-P_4S_{10} (2.2 g) in boiling THF (100 mL) for 70 minutes, mp and mixed mp with an authentic sample 272–274°C.

X-RAY STRUCTURE DETERMINATION OF (**7d**)

Compound (**7d**), $C_{34}H_{30}N_2O_2S_3$, was recrystallized from benzene to give an orange-yellow chunklike crystal (0.48 × 0.44 × 0.38 mm) suitable for an X-ray structure determination. The compound crystallized in space group $P2_1/c$, monoclinic, a = 11.351 (3) Å, b = 20.804 (5) Å, c = 14.162 (5) Å, β = 111.68 (2)°, V = 3107.7 (16) Å^3, Z = 4, D_{calcd} = 1.271 g/cm^{-3}. A Siemens *R*3m/V diffractometer was used with graphite-monochromated Mo K_α radiation (λ 0.71073 Å, μ = 2.6 cm^{-1}, $F(000)$ = 1248): $\theta/2\theta$ technique; scan with 1.00° + K_α separation; scan speed 2.93–14.65° min^{-1}. Cell parameters were determined from least-squares procedure on 15 reflections ($11.73 \leq 2\theta \leq 25.30°$). A total of 5984 reflections were measured up to 2θ = 50.0°. There was no significant variation in intensities of three standards monitored every 50 reflections. Unique structure amplitudes (2759) with $I \leq 3.0\ \sigma(I)$ were corrected for absorption [13], Lorentz, and polarization effects. The structure was solved by direct methods and refined with full-matrix least squares based on F values. All non-H atoms were refined with anisotropic temperature factors. All the H atoms were calculated and refined with fixed U values (0.08 Å^2). At convergence R = 0.0450, R_w = 0.0473, $w = [\sigma^2(F) + 0.008F^2]^{-1}$, based on counting statistics, $(\Delta/\sigma)_{max}$ = 0.001, S = 1.33, $(\Delta\rho)_{max}$ = 0.20, and $(\Delta\rho)_{min}$ = −0.23 e Å^{-3}. Scattering factors were taken from International Tables 3–8 for X-ray Crystallography (1974, Vol. IV). All calculations were performed on a DEC Micro VAX II computer system using the SHELXTL-plus programs [14].

SUPPLEMENTARY MATERIAL AVAILABLE

Structure factors and expanded tables of bond lengths, bond angles, refined displacement parameter expressions, and positional parameters have been sent to the Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB 1EW, United Kingdom.

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