

## Reaction of Aryl Biphenyl-2-yl Thioketones with Ditosyldiazomethane; Internal Cyclisation of the Thioketone *S*-Methylides to afford Benzo[*c*]thiophene Derivatives. Structure Determination of the Products by Raney Nickel Degradation and X-Ray Crystallographic Analysis

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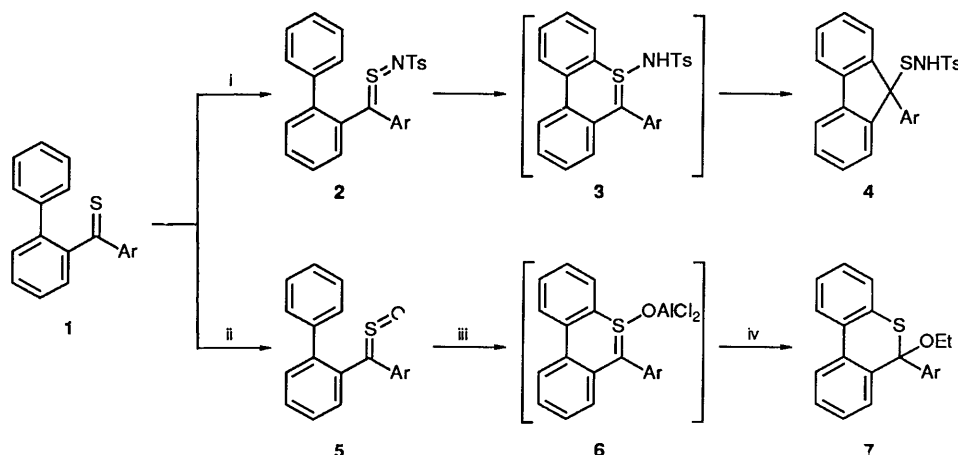
The reaction of arylbiphenyl-2-yl thioketones **1** with ditosyldiazomethane in the presence of copper acetylacetonate has been investigated. It involves internal cycloaddition of intermediary thioketone *S*-methylides **8** and **23** to afford eventually benzo[*c*]thiophene derivatives **16**, and **24** and **25**, respectively. The structure of product **16** was determined by means of spectroscopy and chemical evidence. Furthermore the structure was unambiguously established by X-ray crystallographic analysis of compound **16c** (X = MeO). The results are discussed in terms of cyclisation/rearrangement of the transient thioketone *S*-methylides **8** and **23** as a key step in consideration of the other plausible routes leading to their structural isomers **10**, **11**, **14**, **15** and **17**.

Thiocarbonyl ylides,<sup>1</sup> which may be correlated with other structurally isoelectronic sulphur-centred heterocumulenes with the general formula of X=S=Y,<sup>2</sup> have attracted increasing synthetic and mechanistic attention. These thiocumulenic species are, in general, very reactive and often being unstable eventually decompose and/or give rearranged products which may be trapped *in situ* by appropriate dipolarophiles.<sup>1,2</sup> Among these our target heterocumulenes of choice for inter-comparisons are, in particular, thiocarbonyl *S*-oxides (sulphines), *S*-imides and *S*-methylides since they can be formally (or actually in certain cases) available equally from thiocarbonyl compounds by oxidation, imination and alkylation processes, respectively.

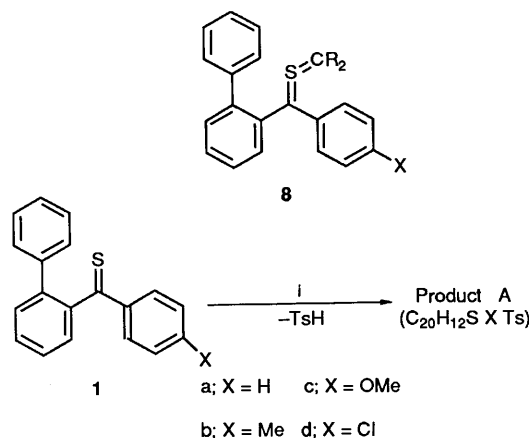
In a previous paper we reported that the thioketone *S*-tosylimides bearing a biphenyl unit **2** underwent electrocyclisation and subsequent Stevens type ring-contraction rearrangement of the intermediary thiaphenanthrenes **3** formed to give *N*-tosylfluorene-9-sulphenamides **4** (Scheme 1).<sup>3</sup> On the other hand, AlCl<sub>3</sub>-catalysed cyclisation of the thioketone *S*-oxides (sulphines) **5** takes place, followed by the Pummerer [1,2]sigmatropic rearrangement of the thiaphenanthrenes **6** to give **7** (Scheme 1).<sup>3</sup> In this context, it is of interest to investigate the behaviour of the corresponding thioketone *S*-methylides **8** in connection with the above results on **2** and **5**.

Tamagaki and Oae reported isolation of stable dithiolethione *S*-ditosylmethylides by treating the thiones with ditosyldiazomethane in the presence of catalytic copper acetylacetonate.<sup>4</sup> Since this procedure is promising for formation of the thioketone *S*-methylides **8**,<sup>1</sup> the reaction of the thioketones **1** with ditosyldiazomethane was performed in a similar manner (Scheme 2). The isolated product **A** has a molecular structure formulated as C<sub>20</sub>H<sub>12</sub>SXTs based on the spectral features (IR, MS, <sup>1</sup>H and <sup>13</sup>C NMR) which indicate a sulphur-containing (hetero)aromatic compound with elimination of one molecule of Ts-H. We had tentatively assigned the structure of **A** as a thiepine **10** or **11** which would have been formed *via* the thiaphenanthrene derivative **9** in the light of the cases of **2** and **5**, as depicted in Scheme 3. If the product **A** is the thiepine **10** or **11**, it should give a phenanthrene derivative **12** with extrusion of sulphur thermally or by the action of a phosphine.<sup>5</sup> However, compound **A** was found to be recovered unchanged after rigorous heating in xylene even in the presence of Ph<sub>3</sub>P.

Recently Hatjiarapoglou and Varvoglis reported the thermal reaction of thiobenzophenones with the carbenoids generated from phenyliodonium disulphonylmethylides in the presence of catalytic Cu(acac)<sub>2</sub> to afford benzo[*b*]thiophene derivatives **13** (Scheme 4).<sup>6</sup> They suggested that the reaction involved



Scheme 1 Reagents: i, Chloramine T; ii, *m*CPBA; iii, AlCl<sub>3</sub>; iv, EtOH



**Scheme 2** Reagents and conditions: i,  $\text{Ts}_2\text{CN}_2/\text{Cu}(\text{acac})_2$  in refluxing benzene, 1 h

rearrangement of the thiocarbonyl ylide moiety to the sulphur-terminated thiaallyl cation ion pair or its congener *via* the thiirane and subsequent cyclisation by the attack of sulphur onto the proximal position of the MeO-substituted arene with a more nucleophilic property. If the reaction of **1** took place similarly, the product **A** would be benzo[*b*]thiophene **14** or **15** (Scheme 5). Again, the thiepine **11** formed *via* the ion pair is also plausible for compound **A**.

Alternative cyclisation may be envisaged which involves direct ylide-carbon attack onto the proximal *ortho*-positions of the arenes to give benzo[*c*]thiophenes **16** or **17** or the thiepine **10** (Scheme 6). We observed weak fluorescence of compounds **A** and this agrees with the observation that many (benzo[*b*]- and [*c*]) thiophene derivatives show fluorescence.<sup>7</sup> However, it is very difficult and risky to distinguish unambiguously among the structures **10**, **11**, **14**, **15**, **16** and **17** by spectroscopic means only.\*

Then, structural determination of compound **A** (X = MeO) was achieved by means of a Raney Ni degradation procedure, the four differently Me-substituted arylbiphenylmethanes **18**–**21** being expected as the degradation product **B**, respectively (Scheme 7). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **B** (X = MeO)

indicated the presence of a methylene and a methyl group linked to an aromatic ring in addition to a methoxy group (see Experimental section). The mass spectrum showed a molecular ion peak ( $\text{M}^+$ ) and fragment peaks of  $\text{M}^+ - \text{MeOC}_6\text{H}_3\text{Me}$  and  $\text{M}^+ - \text{biphenyl}$ . These spectral data agree with only structure **20** (X = MeO), suggesting that compound **A** has structure **16**.<sup>†</sup> Furthermore, to confirm unequivocally structure **16**, an X-ray crystallographic analysis of **16c** has been performed (*vide infra*).

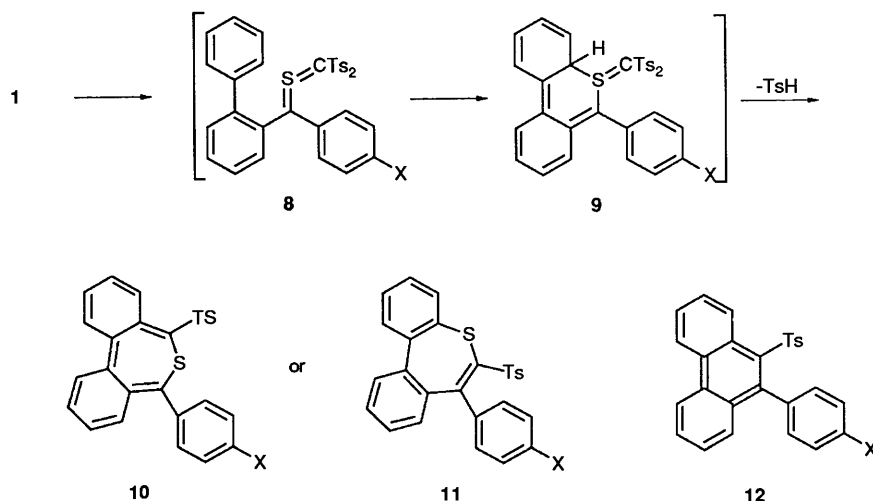
Since certain thiocumulenes carrying bulky substituent(s) such as a mesityl at least or a much bulkier group (e.g., 2,4,6-tri-*tert*-butylphenyl) are known to be sufficiently stabilised for the isolation as far as reported in the literatures,<sup>2</sup> a mesityl substituent was introduced in this case in order to allow isolation as well as to prevent the internal cyclisation of the thio ketene *S*-ylide **23**. Nevertheless, the reaction of thioketone **22** at the similar conditions afforded the thiophene derivatives **24** and **25** in 16 and 60% yields, respectively. The Raney nickel degradation procedure (**24**→**26** and **25**→**27**) and the spectral data (see Experimental section) proved both of the products to be the benzo[*c*]thiophenes **24** and **25**. It is clear that the former thiophene **24** was formed *via* route A after loss of methyl toluene-*p*-sulphinate and that the latter *via* route B, as illustrated in Scheme 8. It is noteworthy that, although the ylide carbon attack onto the *ortho* position of the biphenyl group leading to **25** *via* route B was favoured over that *via* route A due mainly to the steric hindrance, still such disadvantageous attack leading to **24** was actually observed.

#### X-Ray Structure Determination of Benzo[*c*]thiophene **16c**.—

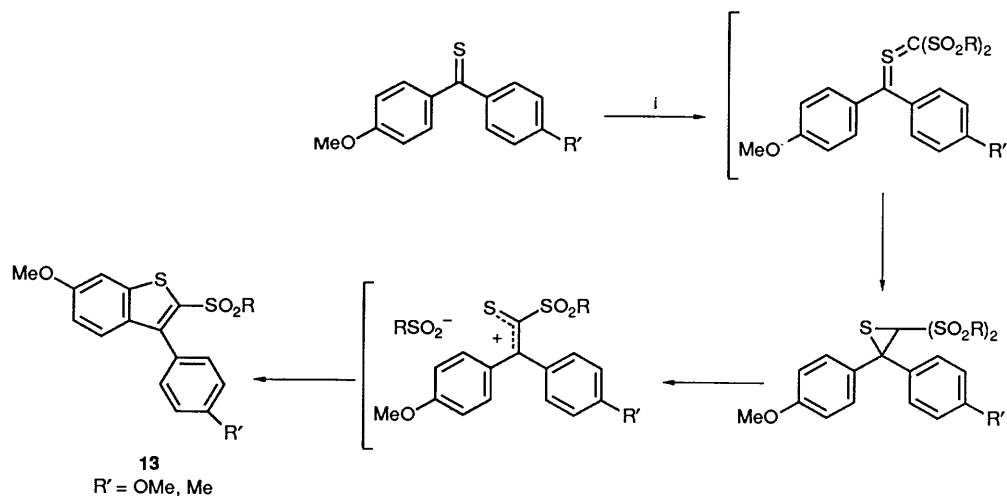
The structure of a single molecule of **16c** is depicted in Fig.1 together with the numbering system adopted. The molecule possesses the following stereochemically characteristic features. (i) The fused benzene and thiophene rings are fairly planar and both on a same plane. (ii) The biphenylphenylene ring is twisted out of the plane of the benzo[*c*]thiophene ring by the dihedral angle of 123.85(8)° with the phenyl group in the opposite direction to the tosyl-tolyl group. (iii) One of the S=O bonds is situated on the plane of the benzo[*c*]thiophene ring, indicating considerable resonance contribution through the

\* This is not the case that there is no hint for the discrimination. For example, in the <sup>1</sup>H NMR spectrum of **A** absence of double doublet coupling signals characteristic of the *para*-substituted phenylene ring protons (typically in case of X = MeO) which should exist in structures **10**, **11**, **15** and **17**, suggests structures **14** and **16** as the candidates.

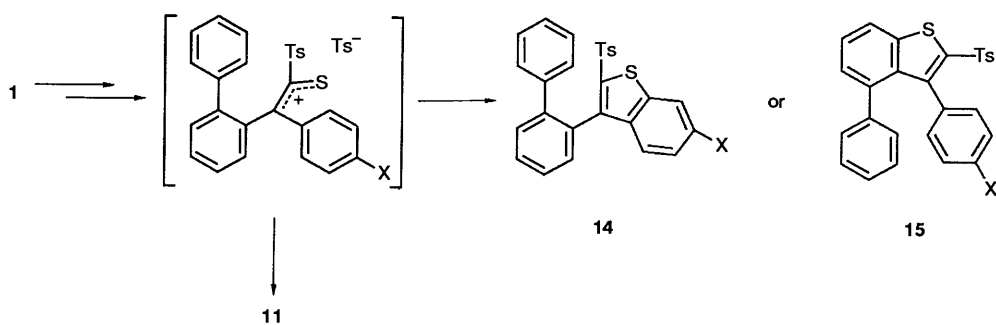
† Reinvestigation of the reaction of simple thiobenzophenones with the carbenoid generated from disulphonyldiazomethane has revealed that the products are not benzo[*b*]thiophenes but benzo[*c*]thiophenes, of which the properties (m.p., IR, UV and NMR) coincide with those as far as reported as benzo[*b*]thiophenes by Hatjjarapoglou and Varvoglis. Details will be reported in a forthcoming publication.



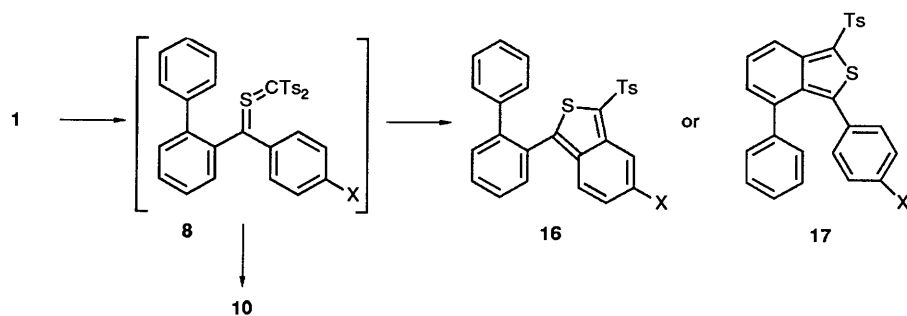
**Scheme 3**



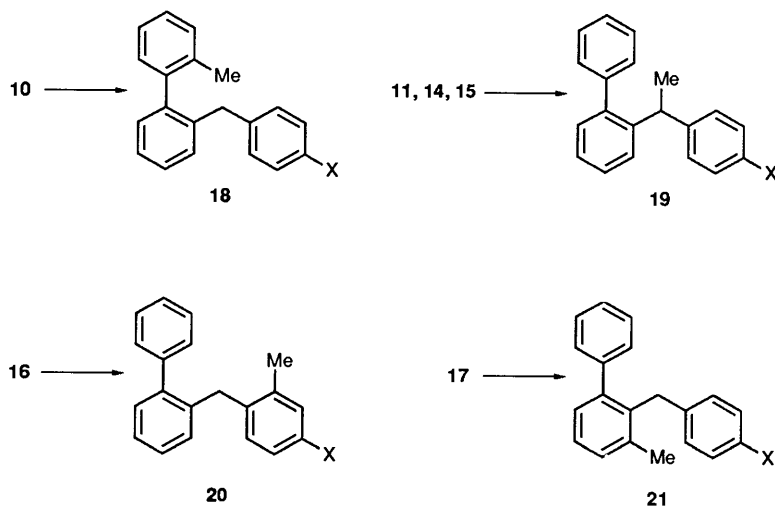
Scheme 4 Reagents and conditions: i, PhI<sup>+</sup> - C<sup>-</sup>(SO<sub>2</sub>R)<sub>2</sub>, Cu(acac)<sub>2</sub>, heat



Scheme 5



Scheme 6



Scheme 7

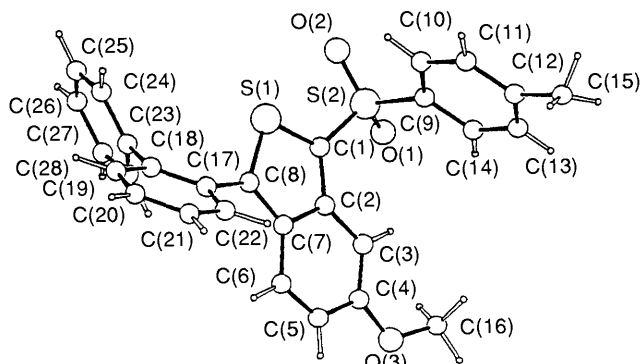


Fig. 1 The molecular structure of the benzo[*c*]thiophene derivative **16c**

Table 1 Benzo[*c*]thiophenes **16**, **24** and **25**

Thioketone	Benzo[ <i>c</i> ]thiophene	Isolated yield (%)
<b>1a</b>	<b>16a</b>	68
<b>1b</b>	<b>16b</b>	60
<b>1c</b>	<b>16c</b>	69
<b>1d</b>	<b>16d</b>	61
<b>22</b>	<b>24</b>	16
	<b>25</b>	60

conjugation. (iv) In Table 2 are listed the selected bond distances and angles within the benzo[*c*]thiophene skeleton comparable with the calculated<sup>8</sup> or experimentally (microwave,<sup>9</sup> X-ray<sup>10</sup>) derived values in the literature.

In conclusion, we have shown that the reaction of aryl biphenyl thioketones with ditosyldiazomethane in the presence of copper(II) catalyst involves transient formation of the thioketone *S*-methylides which show different behaviour in the site selectivity of cyclisation from those of the isoelectronic analogues, thioketone *S*-imides and *S*-oxides, yielding eventually the benzo[*c*]thiophene compounds.

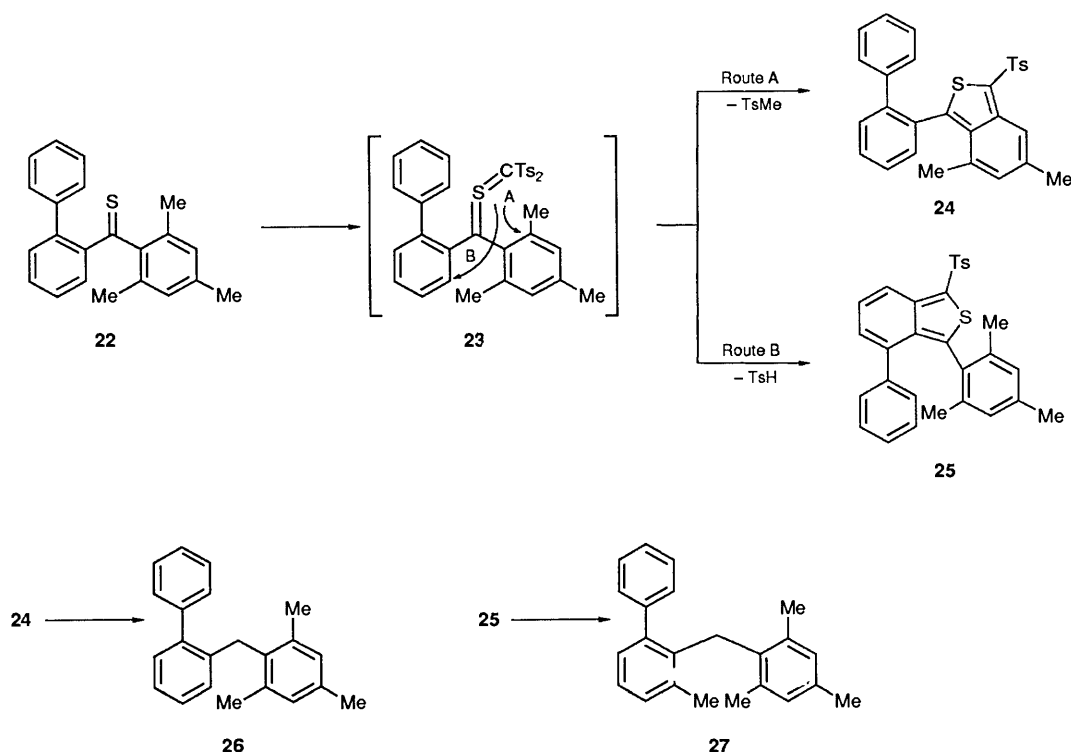
## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded variously on JEOL JNM-PX 60 (60 MHz), JEOL JNM-FX 100 (100 MHz) and JEOL GSX-500 (500 MHz) spectrometers in CDCl<sub>3</sub> using tetramethylsilane as an internal standard. *J* values in Hz. IR spectra were obtained with a Hitachi Model 270-30 spectrometer. UV spectra were recorded on a Hitachi Model 220A spectrometer. Mass spectra were measured on a Hitachi Model RMU-7M double focusing mass spectrometer and/or a M-80 spectrometer with a data processing system M-003. Elemental analyses were performed using a Yanaco MT-3 CHN recorder. Starting materials, aryl biphenyl-2-yl ketones<sup>11</sup> and thioketones<sup>3</sup> **1** and **22** and ditosyldiazomethane,<sup>12</sup> were prepared by the method reported in the literature.

*Reaction of Aryl Biphenyl-2-yl Thioketones 1 with Ditosyldiazomethane in the Presence of Copper Acetylacetonate. General procedure.*—A mixture of aryl biphenyl-2-yl thioketone **1** (1 mmol), ditosyldiazomethane (1.5 mmol) and copper acetylacetonate (10 mg) was heated in dry benzene (20 ml) for 1–1.5 h (for **22** 38 h) at 80 °C under a nitrogen atmosphere. After cooling, the mixture was evaporated under reduced pressure and the residue was chromatographed on silica gel with benzene–hexane (1:1–2) as eluent. From coloured fractions benzo[*c*]thiophenes **16**, **24** and **25** were obtained as yellow greenish fluorescent oils which on storage in a refrigerator solidified for **16a**, **b**, **d** and **24** or crystallized for **16c** and **25**.

1-(Biphenyl-2-yl)-3-tosylbenzo[*c*]thiophene **16a** (299 mg, 68%) (Found: C, 73.95; H, 4.7%; M<sup>+</sup>, 440.0901. C<sub>27</sub>H<sub>20</sub>O<sub>2</sub>S<sub>2</sub> requires C, 73.6; H, 4.6%; M, 440.0906); ν<sub>max</sub>(NaCl)/cm<sup>-1</sup> 1320, 1150 and 1090 (SO<sub>2</sub>); δ<sub>H</sub> 2.35 (3 H, s, CH<sub>3</sub>) and 6.80–8.08 (17 H, m, ArH); δ<sub>C</sub> 21.5 (CH<sub>3</sub>) and 119.8–144.8; *m/z* 440 (M<sup>+</sup>, 90%), 284 (100), 252 (85) and 239 (21).

1-(Biphenyl-2-yl)-5-methyl-3-tosylbenzo[*c*]thiophene **16b** (272 mg, 60%) (Found: M<sup>+</sup>, 454.1048. C<sub>28</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub> requires M, 454.1063); ν<sub>max</sub>(NaCl)/cm<sup>-1</sup> 1320, 1150 and 1085 (SO<sub>2</sub>); δ<sub>H</sub> 2.35 (6 H, s, CH<sub>3</sub>) and 6.72–7.80 (16 H, m, ArH); δ<sub>C</sub> 22.1 (CH<sub>3</sub>), 22.5



Scheme 8

**Table 2** Geometrical parameters for benzo[*c*]thiophene

Selected bond distances (Å) and angles (°) with esds of <b>13c</b>	Reference values				
	lit. 8	lit. 9	lit. 10		
S(1)–C(1) 1.719(2)	S(1)–C(8) 1.715(3)	1.714	1.714	1.726(4)	1.711(4)
C(1)–C(2) 1.392(3)	C(7)–C(8) 1.388(3)	1.371	1.370	1.403(5)	1.398(5)
C(2)–C(3) 1.420(3)	C(6)–C(7) 1.429(4)	1.421	—	1.422(5)	1.420(6)
C(3)–C(4) 1.365(4)	C(5)–C(6) 1.346(4)	1.364	—	1.355(6)	1.354(6)
C(2)–C(7) 1.437(3)		1.418	1.423	1.449(5)	
C(4)–C(5) 1.433(4)		1.415	—	1.446(6)	
C(1)–S(1)–C(8) 92.56(12)		—	92.17	93.7(2)	
S(1)–C(1)–C(2) 112.35(18)	C(7)–C(8)–S(1) 113.58(22)	—	111.47	110.5(3)	111.5(3)
C(1)–C(2)–C(7) 110.59(21)	C(2)–C(7)–C(8) 110.92(18)	—	112.45	112.5(3)	111.9(3)

**Table 3** Atomic parameters

Positional parameters for non-hydrogen atoms are multiplied by  $10^5$ . The equivalent isotropic temperature factor is defined by:

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	34 601(3)	20 328(6)	17 517(3)
S(2)	26 330(3)	38 722(6)	22 813(3)
O(1)	23 995(8)	50 693(17)	20 817(9)
O(2)	21 828(8)	28 547(17)	21 717(9)
O(3)	45 464(10)	73 641(18)	18 014(11)
C(1)	33 109(10)	35 281(21)	19 243(11)
C(2)	38 229(10)	43 000(21)	18 243(10)
C(3)	38 755(11)	55 841(23)	19 045(11)
C(4)	44 266(13)	61 484(25)	17 638(12)
C(5)	49 484(13)	54 736(27)	15 543(13)
C(6)	49 107(11)	42 562(26)	14 745(12)
C(7)	43 406(10)	36 206(22)	16 068(10)
C(8)	42 107(10)	23 799(23)	15 433(11)
C(9)	29 760(11)	39 403(22)	30 966(11)
C(10)	31 114(14)	28 594(25)	34 330(13)
C(11)	34 406(16)	29 133(30)	40 507(14)
C(12)	36 321(14)	40 119(32)	43 445(14)
C(13)	34 737(15)	50 756(29)	40 026(14)
C(14)	31 507(13)	50 558(24)	33 805(13)
C(15)	40 170(20)	40 672(44)	50 110(16)
C(16)	41 030(18)	81 128(28)	20 773(18)
C(17)	56 566(11)	14 129(23)	13 812(11)
C(18)	44 733(12)	5 504(24)	9 010(12)
C(19)	49 293(14)	–3 616(27)	8 163(14)
C(20)	55 496(14)	–4 130(29)	11 967(15)
C(21)	57 329(13)	4 397(29)	16 634(14)
C(22)	52 912(12)	13 507(27)	17 564(13)
C(23)	38 193(13)	5 739(26)	4 659(12)
C(24)	34 212(15)	–4 602(30)	3 977(14)
C(25)	28 197(17)	–4 621(35)	311(17)
C(26)	26 277(16)	5 396(39)	–3 902(15)
C(27)	30 164(16)	15 727(37)	–3 254(15)
C(28)	36 094(14)	15 981(30)	1 071(14)

(CH<sub>3</sub>) and 118.1–143.3; *m/z* 454 (M<sup>+</sup>, 89%), 298 (100), 266 (77) and 239 (38).

1-(Biphenyl-2-yl)-5-methoxy-3-tosylbenzo[*c*]thiophene **16c** (324 mg, 69%), m.p. 177.5–178 °C (from benzene–cyclohexane) (Found: C, 71.6; H, 4.8%; M<sup>+</sup>, 470.1006. C<sub>28</sub>H<sub>22</sub>O<sub>3</sub>S<sub>2</sub> requires C, 71.5; H, 4.7%; M, 470.1012); λ<sub>max</sub>(KBr)/cm<sup>–1</sup> 1303, 1147 and 1086 (SO<sub>2</sub>); λ<sub>max</sub>(EtOH)/nm 233 (25 700), 330 (8700) and 377 (12 900); δ<sub>H</sub> 2.35 (3 H, s, CH<sub>3</sub>), 3.88 (3 H, s, OCH<sub>3</sub>) and 6.56–7.97 (16 H, m, ArH); δ<sub>C</sub> 21.4 (CH<sub>3</sub>), 55.3 (OCH<sub>3</sub>) and 120.1–159.8; *m/z* 470 (M<sup>+</sup>, 100%), 314 (22), 282 (18), 271 (29) and 239 (41).

1-(Biphenyl-2-yl)-5-chloro-3-tosylbenzo[*c*]thiophene **16d** (289 mg, 61%) (Found: M<sup>+</sup>, 474.0494. C<sub>27</sub>H<sub>19</sub>ClO<sub>2</sub>S<sub>2</sub> requires M, 474.0517); ν<sub>max</sub>(NaCl)/cm<sup>–1</sup> 1325, 1147 and 1087 (SO<sub>2</sub>); λ<sub>max</sub>(EtOH)/nm 205 (52 500), 313 (5000), 325 (5500) and 375

(9800); δ<sub>H</sub> 2.36 (3 H, s, CH<sub>3</sub>) and 6.80–8.06 (16 H, m, ArH); δ<sub>C</sub> 21.5 (CH<sub>3</sub>) and 118.5–145.8; *m/z* 474 (M<sup>+</sup>, 100), 318 (89), 286 (67) and 239 (45).

3-(Biphenyl-2-yl)-4,6-dimethyl-1-tosylbenzo[*c*]thiophene **24** (75 mg, 16%) (latter fraction) (Found: M<sup>+</sup>, 468.1233. C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub> requires M, 468.1219); δ<sub>H</sub> 2.02 (3 H, s, CH<sub>3</sub>), 2.30 (3 H, s, CH<sub>3</sub>), 2.35 (3 H, s, CH<sub>3</sub>), 6.60 (1 H, s, ArH) and 7.00–7.80 (14 H, m, ArH); δ<sub>C</sub> 21.1 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 22.8 (CH<sub>3</sub>) and 116.5–144.8; *m/z* 468 (M<sup>+</sup>, 100%), 312 (70) and 239 (11).

3-Mesityl-4-phenyl-1-tosylbenzo[*c*]thiophene **25** (289 mg, 60%) (former fraction), m.p. 199.5–200.5 °C (from benzene–ethyl acetate) (Found: C, 74.5; H, 5.3%; M<sup>+</sup>, 482.1355. C<sub>30</sub>H<sub>26</sub>O<sub>2</sub>S<sub>2</sub> requires C, 74.65; H, 5.4%; M, 482.1376); δ<sub>H</sub> 1.79 (6 H, s, *o*-CH<sub>3</sub>), 2.37 (3 H, s, CH<sub>3</sub>), 6.50 (2 H, s, *m*-H), 6.86 (6 H, m), 7.28 (1 H, d, *J* 4.0), 7.23–7.38 (2 H, m), 7.94 (2 H, d, *J* 4.0) and 8.15 (1 H, dd, *J* 4.0 and 1.5); δ<sub>C</sub> 20.86 (CH<sub>3</sub>), 21.59 (CH<sub>3</sub>) and 119.5–144.7; *m/z* 482 (M<sup>+</sup>, 100%), 239 (3) and 119 (6).

*Raney Ni Degradation of 1-(Biphenyl-2-yl)-5-methoxy-3-tosylbenzo[*c*]thiophene 16c.*—A mixture of **16c** (611 mg, 1.3 mmol) and Raney Ni (W-2, 7.5 g)<sup>13</sup> was heated in ethanol (20 mol) for 2 h under a nitrogen atmosphere. After cooling, the mixture was filtered using Celite. The filtrate was concentrated and chromatographed using ethyl acetate–hexane as eluent to give biphenyl-2-yl (4-methoxy-2-methylphenyl)methane **20** (367 mg, 98%) as colourless needles (from benzene–hexane), m.p. 115–115.5 °C (Found: C, 87.3; H, 7.15%; M<sup>+</sup>, 288.1514. C<sub>21</sub>H<sub>20</sub>O requires C, 87.5; H, 7.0%; M, 288.1515); ν<sub>max</sub>(KBr)/cm<sup>–1</sup> 3080–3000, 2960–2925 and 1618; δ<sub>H</sub> 1.97 (3 H, s, CH<sub>3</sub>), 3.69 (3 H, s, OCH<sub>3</sub>), 3.79 (2 H, s, CH<sub>2</sub>), 6.59 (1 H, d, *J* 7.5), 6.63 (1 H, s), 6.84 (1 H, d, *J* 7.5) and 6.92–7.30 (9 H, m); δ<sub>C</sub> 19.7 (CH<sub>3</sub>), 36.1 (OCH<sub>3</sub>), 55.0 (CH<sub>2</sub>) and 110.7–157.9; *m/z* 288 (M<sup>+</sup>, 99%), 165 (M<sup>+</sup> – CH<sub>3</sub>OC<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>, 100) and 135 (M<sup>+</sup> – biphenyl, 27).

*Raney Ni Degradation of 3-(Biphenyl-2-yl)-4,6-dimethyl-1-tosylbenzo[*c*]thiophene 24.*—A mixture of **24** (201 mg, 0.43 mmol) and Raney Ni (W-2, 4 g) was heated in ethanol–benzene (50 ml) for 32 h under a nitrogen atmosphere. Work-up as described above gave biphenyl-2-ylmesitylmethane **26** (97 mg, 79%) as colourless oil (Found: M<sup>+</sup>, 286.1722. C<sub>22</sub>H<sub>22</sub> requires M, 286.1723); δ<sub>H</sub> 2.08 (6 H, s, *o*-CH<sub>3</sub>), 2.24 (3 H, s, *p*-CH<sub>3</sub>), 3.83 (2 H, s, CH<sub>2</sub>), 6.80 [2 H, s, *m*-H (Mes)] and 6.96–7.48 (9 H, m, ArH); δ<sub>C</sub> 20.0 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 32.6 (CH<sub>2</sub>) and 125.6–142.1; *m/z* 286 (M<sup>+</sup>, 93%), 166 (M<sup>+</sup> – MesH, 24), 165 (M<sup>+</sup> – MesH – H, 100) and 133 (MesCH<sub>2</sub><sup>+</sup>, 11).

*Raney Ni Degradation of 3-Mesityl-4-phenyl-1-tosylbenzo[*c*]thiophene 25.*—A mixture of **25** (627 mg, 1.3 mmol) and Raney Ni (W-2, 4 g) was heated in ethanol–benzene (50 ml) for 35 h under a nitrogen atmosphere. Work-up as described above and chromatography [silica gel, benzene–hexane (1:1)] gave

mesityl(6-methylbiphenyl-2-yl)methane **27** (367 mg, 94%) as a colourless solid, m.p. 101.5–103°C (Found:  $M^+$ , 300.1883.  $C_{23}H_{24}$  requires  $M$ , 300.1879);  $\delta_H$  1.94 [6 H, s, *o*-CH<sub>3</sub> (Mes)], 1.97 (3 H, s, CH<sub>3</sub>), 2.17 (3 H, s, *p*-CH<sub>3</sub>), 4.02 (2 H, s, CH<sub>2</sub>), 6.63 [2 H, s, *m*-H (Mes)] and 6.92–7.36 (8 H, m, ArH);  $\delta_C$  20.4 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 32.4 (CH<sub>2</sub>), 125.6–143.2;  $m/z$  300 ( $M^+$ , 100%), 285 ( $M^+ - CH_3$ , 8), 180 ( $M^+ - MesH$ , 93) and 133 ( $MesCH_2^+$ , 19).

*X-Ray Crystallographic Analysis of 16c.*—Crystal data.  $C_{28}H_{22}O_3S_2$ ,  $M = 470.58$ . Monoclinic,  $a = 20.464(15)$ ,  $b = 10.960(3)$ ,  $c = 21.401(7)$  Å,  $\beta = 99.97(4)^\circ$ ,  $V = 4727$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 8$ ,  $D_x = 1.322$  Mg m<sup>-3</sup>. Yellow plates. Crystal dimensions  $0.72 \times 0.58 \times 0.18$  mm,  $\mu(Mo-K\alpha) = 2.42$  cm<sup>-1</sup>,  $F(000) = 1968$ .

*Data collection and processing.* Enraf-Nonius CAD-4 diffractometer,  $\omega$  scan mode ( $h$ ,  $-26$  to  $26$ ,  $k$ ,  $0$  to  $14$ ,  $l$ ,  $0$  to  $27$ ;  $4^\circ < 2\theta < 55^\circ$ ), graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), 4363 reflections measured, 4214 unique reflections.

*Structure analysis and refinement.* The structure solved by direct method using MULTAN78, refined by block-diagonal least squares with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms located from difference Fourier maps. Final  $R$  and  $R_w$  values are 0.045, 0.041.

The atomic scattering factors and  $f'$ ,  $f''$  values were taken from 'International Tables for X-Ray Crystallography'.<sup>14</sup> The calculations were carried out on a FACOM M-780 computer using UNICS III<sup>15</sup> and ORTEP<sup>16</sup> programs.

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Paper 0/05819J

Received 28th December 1990

Accepted 16th January 1991