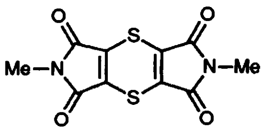
Novel Maleimide-type Acceptors Based on Annelated 1,4-Dithiins

Thomas K. Hansen,[a] Sukumar K. Varma,[b] Stephen Edge,[b] Adam Charlton,[b] Allan E. Underhill[b] and Jan Becher*[a]
[a] *Department of Chemistry, Odense University, DK-5230 Odense M, Denmark*
[b] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*

Bis(tetraethylammonium) bis-(2-thioxo-1,3-dithiole-4,5-dithiolato)zincate(II) **5** reacted with a range of 3,4-dichloromaleimides **4** (R = H, alkyl or aryl) to give a new annelated 1,4-dithiin system **6** in high yield. Oxidation of the thiones **6** gives the corresponding [1,3]-dithiolones **7**. Cyclic voltammetry indicates that the new compounds are electron acceptors.

Although the parent 1,4-dithiin ring system is conformationally mobile,[1] a different electron distribution and geometry can be expected of derivatives of the parent system. Indeed, our interest in fused dithiin systems was stimulated by Draber's report[6] of the crystalline charge-transfer (CT) complex (1:1) formed by the reaction of 1,4-dithiintetracarboxylic *N,N'*-dimethyldiimide **1** with acridine and the subsequent X-ray structure determination by Yamaguchi *et al.*[3] which showed that the dithiin ring was planar in this complex. Later, our X-ray diffraction study[5] of the [1,4]dithiino[2,3-*b*][1,4]dithiin[5,6] **2**, showed that this mono-annelated system has non-planar dithiin rings. Although the CT complex formed from the electron acceptor **1** and acridine showed no significant electrical conductivity,[4] CT-complexes of related 1,4-dithiins with appropriate electron donors might have interesting solid state properties.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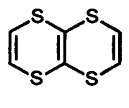
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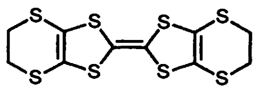
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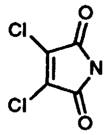
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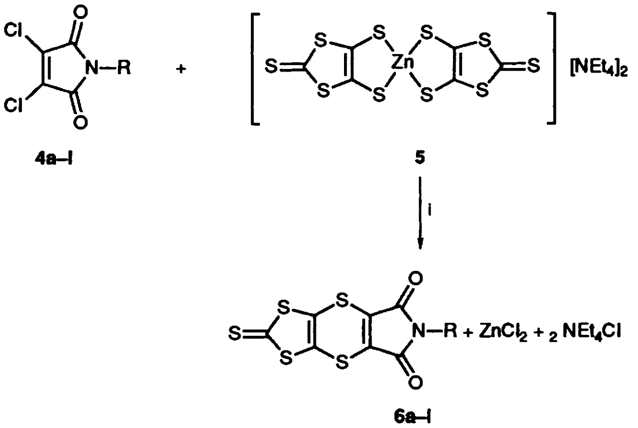
Since the 3- and 4-halogeno substituents in the starting maleimides **4** are reactive towards sulfur nucleophiles,[7] the fused dithiin system **1** was prepared directly from hydrogen sulfide and dichloromaleimide **4**.

The organic π-donor, BEDT-TTF **3** and related systems have been the subject of numerous studies as some of its salts show superconducting properties.[8,9] It has recently been demonstrated[10] that the incorporation of heterocyclic moieties in multisulfur donors results in enhanced intra-stack interaction *via S–N* contacts. Yamashita *et al.*[11] have reported that a number of *p*-benzoquinone derivatives fused with sulfur-containing heterocycles such as dithiins results in annelated systems which are electron acceptors and these compounds show intermolecular sulfur–sulfur contacts in the solid state. As noted by Yamashita *et al.*[11] electron acceptors containing sulfur atoms are rare and are naturally of interest because of possible solid-state interactions. Consequently, it was of interest to investigate the preparation of the hitherto unknown annelated dithiin system **6** using readily available dichloromaleimides[12] and the zincate **5**[13] (Scheme 1).



	R		R
a	H	**g**	C_6H_4Ac-*p*
b	Et	**h**	C_6H_4OMe-*p*
c	$[CH_2]_5Me$	**i**	$C_6H_4NO_2$-*p*
d	C_6H_4Bu-*p*	**j**	$C_6H_4CF_3$-*m*
e	$C_6H_4Bu^t$-*p*	**k**	$CH_2C_6H_5$
f	C_6H_4Cl-*p*	**l**	Me

Scheme 1 *Reagents and conditions:* i, THF, 25 °C

Results and Discussion

The new dithiins **6** were prepared by direct reaction of the zinc complex **5** with the appropriate 3,4-dichloromaleimide **4** in dry tetrahydrofuran (THF) under nitrogen at room temperature. Thus addition of compound **4** to a red suspension of the complex **5** gave, within a few minutes, dark solutions from which the crystalline products were usually precipitated. Although with the more reactive disodium 2-thioxo-1,3-thiole-4,5-dithiolate[11] instead of the zinc complex **5** extensive polymerisation took place at room temperature, at very low temperature (< − 100 °C) it worked equally well.

The crystalline reaction products **6** are polymorphous and were obtained either as transparent red plates or as dark green or brownish green opaque crystals. In some cases the initial precipitate was green which upon recrystallisation formed the red crystalline modification. In one case, (compound **6h**) a mixture of the two types of crystals were obtained after recrystallisation from THF, the spectroscopic data for the two being identical but their melting points differed by 1 °C.

Oxidation of the thiones **6** with mercury(II) acetate gave the corresponding 1,3-dithiole-2-ones **7**[14] (Scheme 2).

Normally 1,3-dithiole-2-thiones are yellow to orange compounds and conversion into the 1,3-dithiole-2-ones results in

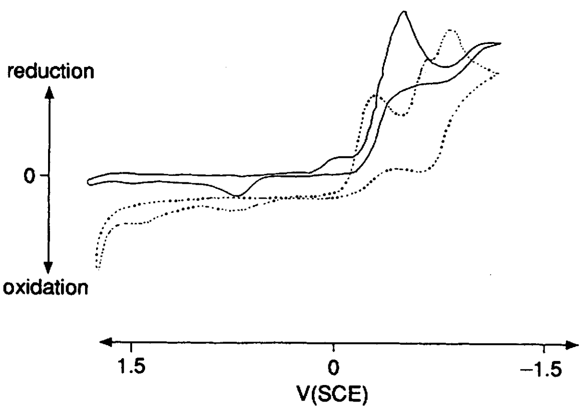
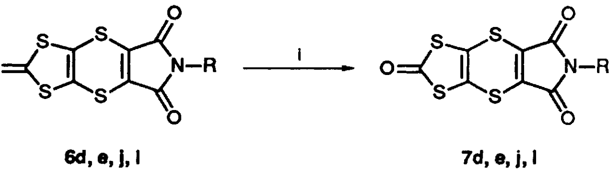


Fig. 1 Cyclic voltammograms of compounds **6d** and **6i**; TBABF$_4$ in CH$_2$Cl$_2$ (0.1 mol dm^{-3}); 50 mV s^{-1}; **6d**, (——); **6i**, (- - - -)

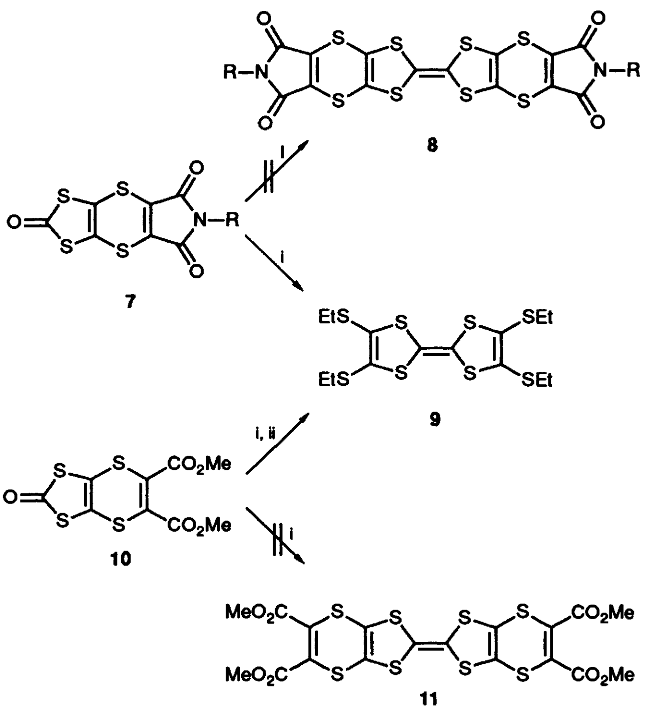


Scheme 2 *Reagents and conditions:* i, Hg(OAc)$_2$, AcOH, CHCl$_3$

colourless or pale yellow materials. However, the oxidation of compounds **6** to the products **7** had a different effect. Oxidation of compound **6d** (red, both in solution and in the solid state) produced an intensely coloured crystalline blue–black compound **7d** which was pink in solution. A similar colour change was observed for compound **6e** (olive green to green–black), but not for compounds **6j** and **6l** which showed almost no change in colour (red) during oxidation. The UV data (see Experimental section) of compound **7d** indicate that the molecule is highly polarisable, but give no indication of a CT transition in solution. Weak absorption at 477.5 nm was concentration independent. However a solid state UV/VIS spectrum of compound **7d** showed strong, broad absorption with λ_{max} 568 nm which covered almost the full visible spectrum. We assume this was due to intermolecular CT in the solid state.

Cyclic voltammograms for two examples are shown in Fig. 1. The main feature is the reduction of the maleimide ring to the radical anion[15,16] at $E = -0.6$ V (SCE) for compound **6c** (R = 4-Bu^{t}C$_6$H$_4$) and at $E = -1.0$ V (SCE) for compound **6i** (R = 4-NO$_2$C$_6$H$_4$). The latter derivative also showed reduction peaks at $E = -0.5$ and -0.9 V (SCE). These latter reduction peaks which were irreversible at the scan rates used during cyclic voltammetry and close to the reported reduction potentials for *p*-dinitrobenzene [$E_1 = -0.5$ V (SCE) and $E_2 = -0.87$ V (SCE)],[17] suggest that compound **6i** behaves in a similar way (see latter compound). Nitrobenzene itself is reduced at -1.1 V (SCE).[18] Based on the cyclic voltammograms of compounds **6c** and **6i** (Fig. 1) it appears that the annelation of the maleinimide ring to the dithiine systems results in an overall decrease in electron density over the multisulfur subunit and therefore allows 'electron-acceptor' type behaviour. It is known[19] that *m*-dinitrobenzene forms insulating adducts with tetrathiafulvalene (TTF). However, attempts to form complexes of compound **6i** with TTF failed.

All attempts to couple the [1,3]dithiole-2-thiones **6** or [1,3] dithiole-2-ones **7** to form TTF-derivatives **8** were unsuccessful. Thus, PPh$_3$ failed to bring about any reaction when refluxed with compounds **6** or **7** in xylene, whereas other coupling reagents [P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$ and Co$_2$(CO)$_8$] generated complicated mixtures. Attempted coupling of compound **7**, gave the known compound **9**[20] in low yield from a complex mixture. This reaction seems related to that in which compound **10** yields the same product **9** instead of the expected TTF derivative **11**.[20] Presumably this reaction proceeds *via* attack of phosphorus on the relatively electrophilic alkene bearing the imide substituent and followed by an Arbuzov rearrangement.



Scheme 3 *Reagents:* i, P(OEt)$_3$; ii, ref. 20

Experimental

General Methods.—M.p.s were performed on a Buchi melting point apparatus and are uncorrected. Microanalyses were carried out by NOVO A/S Bagsværd, Denmark or by Microanalytical Lab., University of Copenhagen. The UV/VIS spectra were recorded on a Varian CARY 219. The IR spectra were obtained on a Perkin-Elmer 580. The EI-mass spectra were recorded on a Varian Mat 311A. NMR spectra were recorded on the following spectrometers: Bruker AC 250, JEOL JNM-PMX 60 or JEOL FX-60Q.

General Procedure for Compounds **6**.—A dichloromaleimide **4a–l** (10.5 nmol) in a 500 cm^3 conical flask was dissolved (in some cases not completely) in dry THF (100 cm^3). With efficient stirring Zn(Et$_4$N)$_2$(dmit)$_2$ **5** (5 nmol, 3.59 g) was added in small portions over 15 min after which the mixture was stirred for a further 15 min; during this period, the colour of the mixture turned from deep red to either deep green or deep brown. The mixture was then slowly diluted with water (300 cm^3) over 1 h after which the resulting voluminous product was filtered off and recrystallised. Compound **6c** separated as a viscous oil and in this case the aqueous phase was extracted with CHCl$_3$ (3 × 75 cm^3). The chloroform phase was dried (CaCl$_2$) and evaporated until the product started to separate as an oil. A small amount of CHCl$_3$ was then added until all the compound redissolved, after which the solution was cooled to -20 °C. The volume of the solution was then increased by 50% by addition of cold absolute ethanol; whereupon the product crystallised slowly on further cooling.

2-Thioxo-6*H*-[1,3]dithiolo[4′,5′:5,6][1,4]dithiino[2,3-*c*]-pyrrole-5,7-dione **6a**. Yield 2.70 g (95%), m.p. 205 °C (decomp.) (EtOH); *m*/*z* (EI) 291 (M$^+$, 48%), 247 (14) and 88 (100); ν_{max}(KBr)/cm^{-1} 1770, 1719 and 1333 (imide) and 1078 (C=S);

δ_H(250 MHz; MeOD; Me$_4$Si) 8.5 (1 H, s, NH) (Found: C, 29.0; H, 0.4; N, 4.75; S, 54.8. $C_7HNO_2S_5$ requires C, 28.87; H, 0.34; N, 4.81; S, 54.98%).

6b. Yield 1.20 g (37%), m.p. 160–162 °C (EtOH); *m/z* (EI) 319 (M$^+$, 81%), 275 (18) and 88 (100); ν_{max}(KBr)/cm^{-1} 1773, 1696 and 1349 (imide) and 1077 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 3.10 (2 H, q, CH$_2$) and 1.22 (3 H, t, CH$_3$) (Found: C, 34.0; H, 1.6; N, 4.3; S, 49.7. $C_9H_5NO_2S_5$ requires C, 33.86; H, 1.57; N, 4.39; S, 50.16%).

6c. Yield 3.00 g (81%), m.p. 59–60 °C (CHCl$_3$–EtOH); *m/z* (EI) 375 (M$^+$, 39%), 331 (8) and 88 (100); ν_{max}(KBr)/cm^{-1} 1773, 1710 and 1366 (imide) and 1066 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 3.50 (2 H, t, NCH$_2$) and 1.60 (2 H, m, NCH$_2$C*H*$_2$) (Found: C, 41.4; H, 3.5; N, 3.7; S 42.9. $C_{13}H_{13}NO_2S_5$ requires C, 41.58; H, 3.49; N, 3.73; S, 42.69%); δ_C 209.0 (C-2), 163.1 (C-7), 137.7 (C-8a), 120.7 (C-4a), 39.0 (C-1′), 31.0 (C-2′), 28.2 (C-3′), 26.1 (C-4′), 22.3 (C-5′) and 13.8 (C-6′).

6d. Yield 3.63 g (86%), m.p. 161 °C (CHCl$_3$–MeOH); *m/z* (EI) 423 (M$^+$, 47%), 380 (10) and 132 (100); ν_{max}(KBr)/cm^{-1} 1775, 1715 and 1383 (imide) and 1083 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.30 (2 H, d, Ph), 7.20 (2 H, d), 2.15 (2 H, t, PhCH$_2$), 1.60 (2 H, m, PhCH$_2$C*H*$_2$), 1.38 (2 H, m, PhCH$_2$CH$_2$C*H*$_2$) and 0.95 (3 H, t, CH$_3$); λ_{max}(EtOH–MeCN, 1:1)/nm 223.5 (ε 2.24 × 10^4), 300.5 (9.44 × 10^3) and 391.5 (9.10 × 10^3) (Found: C, 48.5; H, 3.1; N, 3.4; S, 37.8. $C_{17}H_{13}NO_2S_5$ requires C, 48.2; H, 3.07; N, 3.31; S, 37.83%).

6e. Yield 3.60 g (85%), m.p. 209 °C (CHCl$_3$–light petroleum); *m/z* (EI) 423 (M$^+$, 100%), 408 (82) and 160 (27); ν_{max}(KBr)/cm^{-1} 1779, 1718 and 1379 (imide) and 1075 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.48 (2 H, d, Ph), 7.20 (2 H, d, Ph) and 1.45 (9 H, s, Bu^t) (Found: C, 49.0; H, 3.2; N, 3.3; S, 37.3. $C_{17}H_{13}NO_2S_5$ requires C, 48.2; H, 3.07; N, 3.3; S, 37.83%).

6f. Yield 3.95 g (98%), m.p. 248–250 °C (CHCl$_3$); *m/z* (EI) 401 (M$^+$, 67%), 357 (13) and 88 (100); ν_{max}(KBr)/cm^{-1} 1773, 1723 and 1379 (imide) and 1088 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.60 (2 H, dd, Ph) and 7.45 (2 H, dd, Ph) (Found: C, 39.2; H, 1.0; N, 3.5; S, 39.8. $C_{13}H_4ClNO_2S_5$ requires C, 38.85; H, 1.00; N, 3.48; S, 39.89%).

6g. Yield. 3.80 g (93.0%), m.p. 234 °C (decomp.) (toluene); *m/z* (EI) 409 (M$^+$, 31%), 146 (24) and 88 (100); ν_{max}(KBr)/cm^{-1} 1779, 1721 and 1381 (imide) and 1088 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 8.05 (2 H, d, Ph), 7.50 (2 H, d, Ph) and 2.22 (3 H, s, CH$_3$) (Found: C, 44.2; H, 1.75; N, 3.3; S, 38.9. $C_{15}H_7NO_3S_5$ requires C, 44.01; H, 1.71; N, 3.42; S, 39.12%).

6h. Yield 3.61 g (91%), m.p. 236 °C (green form) 237 °C (red form) (THF); *m/z* (EI) 397 (M$^+$, 23%), 189 (17) and 76 (100); ν_{max}(KBr)/cm^{-1} 1779, 1718 and 1392 (imide) and 1071 (C = S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.22 (2 H, dd, Ph), 6.98 (2 H, dd, Ph) and 3.82 (3 H, s, CH$_3$) (Found: C, 42.5; H, 1.8; N, 3.40; S, 39.7; $C_{14}H_7NO_3S_5$ requires C, 42.32; H, 1.76; N, 3.53; S, 40.30%).

6i. Yield 3.46 g (84%), m.p. 229–231 °C (CHCl$_3$); *m/z* (EI) 412 (M$^+$, 52%), 368 (10) and 88 (100); ν_{max}(KBr)/cm^{-1} 1782, 1724 and 1343 (imide) and 1066 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 8.35 (2 H, d, Ph) and 7.10 (2 H, d, Ph) (Found: C, 37.8; H, 1.0; N, 6.8. $C_{13}H_4N_2O_3S_5$ requires C, 37.85; H, 0.98; N, 6.79%).

6j. Yield, 3.52 g (81%), m.p. 174–176 °C (CHCl$_3$–EtOH); *m/z* (EI) 435 (M$^+$, 100%), 391 (18) and 88 (86); ν_{max}(KBr)/cm^{-1} 1782, 1718 and 1381 (imide) and 1069 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.65 (1 H, s, Ph) and 7.60 (3 H, m, Ph) (Found: C, 38.5; H, 0.9; N, 3.1; S, 36.9. $C_{14}H_4F_3NO_2S_4$ requires C, 38.62; H, 0.92; N, 3.22; S, 37.04%).

6k. Yield: 2.81 g (74%), m.p. 162 °C (CHCl$_3$–EtOH); *m/z* (EI) 381 (M$^+$, 62%), 337 (9) and 91 (100); ν_{max}(KBr)/cm^{-1} 1771, 1713 and 1392 (imide) and 1069 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.30 (5 H, m, Ph) and 4.60 (2 H, s, CH$_2$) (Found: C, 44.0, H, 1.9; S, 41.6. $C_{14}H_7NO_2S_5$ requires C, 44.09; H, 1.84; N, 3.67; S, 41.99%).

6l. Yield: 2.68 g (88%), m.p. 188–190 °C (CHCl$_3$–MeOH); *m/z* (EI) 305 (M$^+$, 100%). ν_{max}(KBr)/cm^{-1} 1771, 1693 and 1381 (imide) and 1068 (C=S); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 3.10 (3 H, s, CH$_3$) (Found: C, 31.0; H, 1.0; N, 4.6; $C_8H_3NO_2S_5$ requires C, 31.48; H, 0.98; N, 4.59%).

General Procedure for the [1,3]*Dithiolo*[4′,5′:5,6][1,4]*dithiino*[2,3-*c*]*pyrrole*-2,5,7-*triones* **7d, e, j, l**.—Hg(OAc)$_2$ (15 g) was mixed with glacial acetic acid (150 cm^3) and CHCl$_3$ (200 cm^3) and the appropriate thione **6d, e, j, l** (0.018 mol) was slowly added and the mixture stirred overnight. The solvent was evaporated off and the residue triturated with CHCl$_3$ (*ca.* 300 cm^3) and the organic phase was washed with water (100 cm^3), aq. Na$_2$CO$_3$ (50 cm^3), with water (2 × 50 cm^3) and then dried (CaCl$_2$). The crude product was recrystallised (CHCl$_3$–MeOH).

7d. Yield 4.82 g (66%), m.p. 188 °C (CHCl$_3$–MeOH); *m/z* (EI) 407 (M$^+$, 100%), 379 (42) and 132 (64%); ν_{max}(KBr)/cm^{-1} 1779, 1714 and 1710 (imide and C=O); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.20 (4 H, dd, Ph), 2.65 (2 H, t, PhCH$_2$), 1.65 (2 H, m, PhCH$_2$C*H*$_2$), 1.37 (2 H, m, PhCH$_2$CH$_2$C*H*$_2$) and 0.90 (3 H, t, CH$_3$); λ_{max}(EtOH–MeCN, 1:1)/nm 259.0 (ε, 10.2 × 10^4) and 225.2 (1 70 × 10^4); λ_{max}(CHCl$_3$)/nm 477.5 (ε, 250), 268.0 (1.14 × 10^4) and 246.5 (1.20 × 10^4) (Found: C, 50.25; H, 3.2; N, 3.3; S, 31.4. $C_{17}H_{13}NO_3S_4$ requires C, 50.12; H, 3.19; N, 3.45; S, 31.45%).

7e. Yield 4.47 g (61%), m.p. 81 °C (CHCl$_3$–MeOH); *m/z* (EI) 407 (M$^+$, 100%), 392 (42) and 364 (50); ν_{max}(KBr)/cm^{-1} 1780 and 1714 (imide) and 1692 (C=O); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.45 (4 H, dd, Ph) and 1.35 (9 H, s, Bu^t) (Found: C, 50.2; H, 3.2; N, 3.4; S, 31.4. $C_{17}H_{13}NO_3S_4$ requires C, 50.12; H, 3.19; N, 3.35; S, 31.45%).

7j. Yield 3.62 g (48%), m.p. 201 °C (CHCl$_3$–MeOH); *m/z* (EI) 419 (M$^+$, 27%), 391 (19) and 88 (100); ν_{max}(KBr)/cm^{-1} 1713 and 1784 (imide) and 1692 (C=O); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 7.65 (4 H, m, Ph) (Found: C, 39.9; H, 0.98; N, 3.4. $C_{14}H_4F_3NO_3S_4$ requires C, 40.09; H, 0.95; N, 3.34%).

7l. Yield 4.21 g (81%), m.p. 180–182 °C (CHCl$_3$–MeOH); *m/z* (EI) 289 (M$^+$, 100%); ν_{max}(KBr)/cm^{-1} 1778, 1713 and 1385 (imide); δ_H(250 MHz; CDCl$_3$; Me$_4$Si) 3.10 (3 H, s, Me) (Found: C, 32.8; H, 0.95; N, 4.7. $C_8H_3NO_3S_5$ requires C, 33.21; H, 1.03; N, 4.63%).

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