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Synthesis and characterization of 9,9-dialkylfluorene capped benzo[*c*]thiophene/benzo[*c*]selenophene analogs as potential OLEDs

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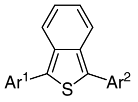
ABSTRACT

The synthesis of soluble benzo[*c*]thiophene analogs capped with 9,9-dialkylfluorene at one end is described.

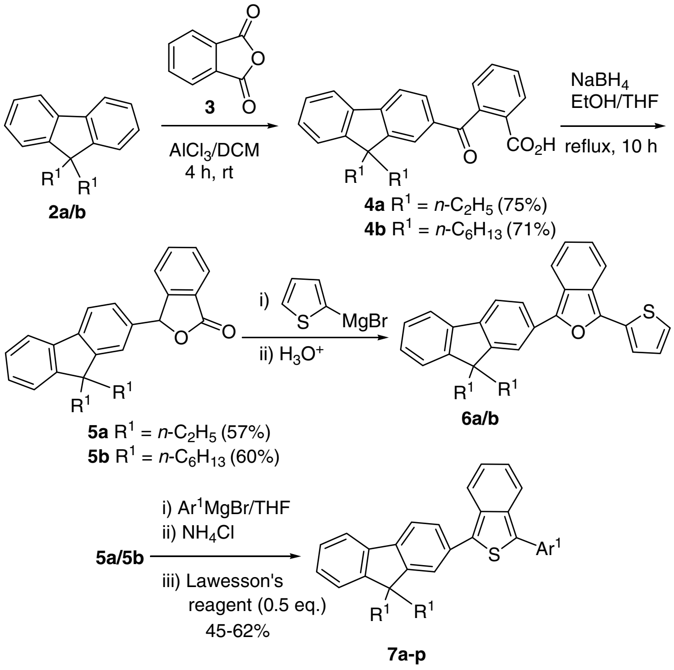
Electronic properties of linear conjugated oligomers have acquired growing importance in many areas of modern chemistry. In particular, π-conjugated thiophene oligomers possess interesting electronic and optical properties and they have been investigated as Organic Field Effect Transistors (OFETs)[1] and Organic Light-Emitting Diodes (OLEDs).[2] Dialkyl/diarylfluorene-containing thienyl oligomers are reported widely in the literature. Bao and co-workers reported the synthesis of fluorene-end capped oligothiophenes which are used as organic thin film transistors.[3] The oligo(fluorenebithiophene)core was found to have high charge transport mobility and good device performance. Lee et al. reported the synthesis of oligo(9,9-dihexyl-2,7-fluorene ethynylene)s as a blue light-emitting diode[4] whilst Pei and co-workers have reported the synthesis of oligothiophene-truxene conjugates.[5] Wong and co-workers reported the synthesis and photophysical studies of 9,9-ditolylfluorene analogs containing thiophene rings.[6]

Numerous examples of benzo[*c*]thiophene **1** (Fig. 1) and its analogs[7] are known in the literature. However, to our knowledge, there are no reports on benzo[*c*]thiophene derivatives capped with fluorene. In continuation of our work on benzo[*c*]thiophenes,[8]



1 $Ar^1 = Ar^2$ = aryl/heteroaryl

Figure 1.



Scheme 1.

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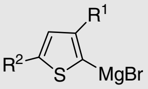
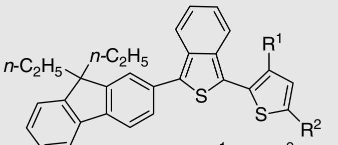
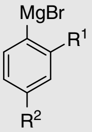
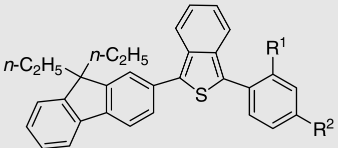
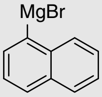
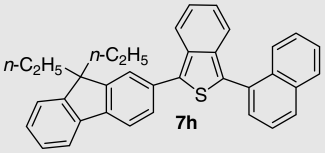
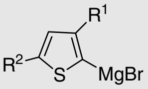
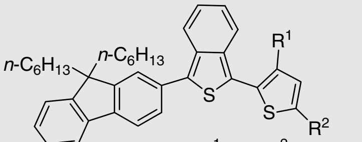
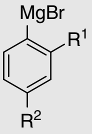
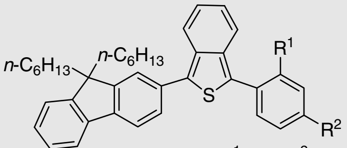
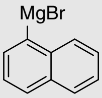
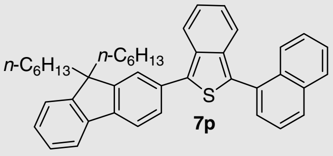
we report here our preliminary results on the synthesis and characterization of 9,9-dialkylfluorene capped benzo[*c*]thiophenes/benzo[*c*]selenophenes.

Friedel–Crafts phthaloylation of 9,9-dialkylfluorenes **2a**–**b**[9] in the presence of anhydrous $AlCl_3$ in DCM at room temperature for 4 h followed by workup led to the isolation of fluorenyl keto-acids **4a**–**b** in good yields. Reduction of the ketone carbonyl of **4a**–**b** using $NaBH_4$ in EtOH/THF at reflux followed by acidic workup furnished the lactones **5a/5b**. Ring-opening of the lactones **5a/b** using freshly prepared 2-thienylmagnesium bromide followed by acidic workup and column chromatographic purification gave the respective benzo[*c*]furans **6a/6b** as orange-yellow solids. The ^{1}H NMR spectral analysis of bright yellow fluorescent solutions of **6a/6b** confirmed that these compounds were highly unstable as the solutions turned red. However, ring-opening of the lactones **5a/b** with aryl/hetero-aryl Grignards[10] followed by quenching with aq NH_4Cl led to the respective keto-alcohols. The DCM solution of keto-alcohol on thionation using 0.5 equiv of Lawesson's reagent followed by in situ intramolecular cyclization and subsequent column chromatographic purification afforded respective benzo[*c*]thiophene

Table 1
Synthesis of benzo[*c*]thiophene analogs containing 9,9-dialkylfluorenes

Entry	Lactone	Ar^1MgBr[10]	Product[11]	Yield (%)[a] mp
1	**5a**		 **7a** R^1 = H, R^2 = H **7b** R^1 = H, R^2 = *n*-C_6H_{13} **7c** R^1 = *n*-C_6H_{13}, R^2 = H	57 (56 °C) 45 (Orange liquid) 57 (Orange liquid)
2	**5a**		 **7d** R^1 = H, R^2 = H **7e** R^1 = Me, R^2 = H **7f** R^1 = H, R^2 = Me **7g** R^1 = H, R^2 = OMe	50 (55 °C) 56 (52 °C) 52 (55 °C) 47 (59 °C)
3	**5a**		 **7h**	52 (Yellow liquid)
4	**5b**		 **7i** R^1 = H, R^2 = H **7j** R^1 = *n*-C_6H_{13}, R^2 = H **7k** R^1 = H, R^2 = *n*-C_6H_{13}	62 (Orange liquid) 57 (Orange liquid) 50 (Orange liquid)
5	**5b**		 **7l** R^1 = H, R^2 = H **7m** R^1 = Me, R^2 = H **7n** R^1 = H, R^2 = Me **7o** R^1 = H, R^2 = OMe	57 (Yellow liquid) 52 (Yellow liquid) 57 (Yellow liquid) 58 (Yellow liquid)
6	**5b**		 **7p**	55 (Yellow liquid)

[a] Isolated yield after column chromatography.

analogs **7a**–**p**[11] as highly stable compounds in 45–62% yields (Scheme 1). The results are presented in Table 1.

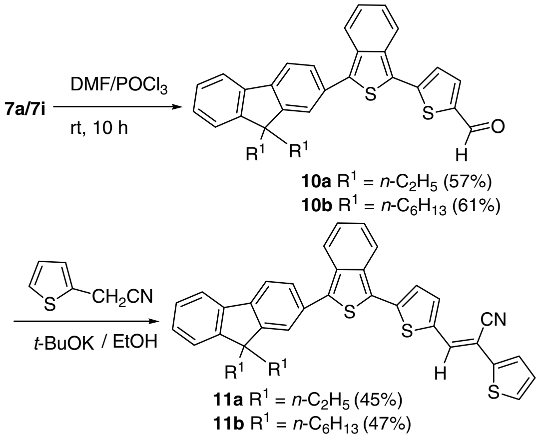
Ring-opening of lactone **5a** with thienyl-2-magnesium bromide followed by thionation afforded 1-(9,9-diethylfluorenyl)-3-thienylbenzo[*c*]thiophene **7a** in 57% yield as an orange solid (Table 1, entry 1). Reaction of lactone **5a** with 5-hexyl-2-thienylmagnesium bromide/3-hexyl-2-thienylmagnesium bromide gave benzo[*c*]thiophenes **7b** and **7c** as orange liquids in 45% and 57% yields, respectively (Table 1, entry 1). Lactone **5a** also underwent similar reaction with aryl Grignards to afford the respective benzo[*c*]thiophenes **7d**-**h** in 47-56% yields (Table 1, entries 2 and 3). Similarly, reaction of 9,9-dihexylfluorenyl lactone **5b** with thienyl Grignards followed by thionation and column chromatographic purification led to the isolation of the corresponding benzo[*c*]thiophenes **7i**–**k** as orange liquids in 50–62% yields (Table 1, entry 4). Similarly, reaction of lactone **5b** with various aryl Grignards also afforded the expected benzo[*c*]thiophenes **7l**–**p** as yellow liquids in 52–58% yields (Table 1, entries 5 and 6).

As a representative case, the ring-opening of the lactone **5b** with various 2-thienylmagnesium bromides followed by acidic workup and subsequent treatment with 0.25 equiv of Woollins reagent adopting our published procedure[12] afforded benzo[*c*]selenophene derivatives **8a**–**c**[13] in 55–62% yields, (Scheme 2). Most of the benzo[*c*]thiophenes **7a**–**p** and benzo[*c*]selenophenes **8a**–**c** were found to be highly soluble in common organic solvents.

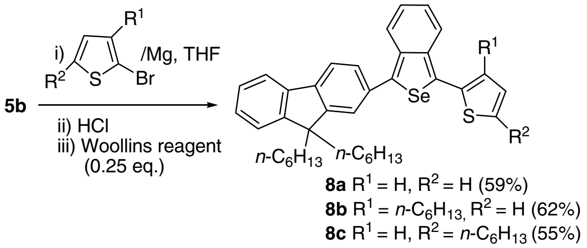
The 9,9-dialkylfluorenyl benzo[*c*]thiophenes **7a/7i** could be converted into the corresponding dimers **9a/9b**[14] in low yields using anhydrous $FeCl_3$ in DCM (Scheme 3).

Finally, Vilsmeier–Haack formylation of **7a/7i** followed by column chromatographic purification afforded aldehydes **10a/b**[15] in 57% and 61% yields, respectively. Condensation of these aldehydes with thiophene-2-acetonitrile afforded the corresponding conjugated cyano-vinylenes **11a/b**[15] (Scheme 4).

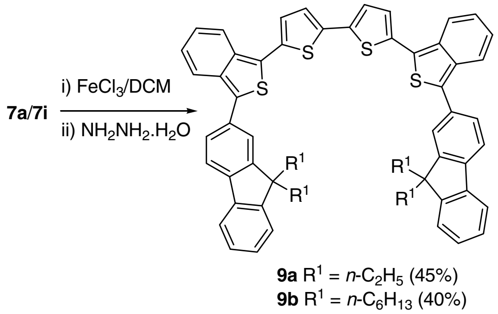
The UV–vis spectra of benzo[*c*]thiophene/benzo[*c*]selenophene analogs exhibited a strong absorption in the region of 425–465 nm due to the π–π^* electronic transition of the conjugated backbone system. The exact λ_{max} values of these compounds are given in Table 2. The qualitative emission data of selected compounds were recorded in DCM solution and the emission values of selected benzo[*c*]thiophene/benzo[*c*]selenophene analogs are also presented. The HOMO and LUMO energy levels of the benzo[*c*]thiophene/benzo[*c*]selenophene analogs were calculated from the absorption onset and the onset oxidation potential. The E_g, HOMO and LUMO values obtained for selected benzo[*c*]heterocycles are presented in Table 2. The monomeric benzo[*c*]thiophene/benzo[*c*]selenophene analogs showed E_g values in the range of 2.5–2.7 eV. The dimerization of benzo[*c*]thiophenes (**7a/i**) as well as the introduction of electron-withdrawing group (**10a/b**) significantly reduced the E_g values. In general, dimerization (**9a/b**) reduced the HOMO energy levels (~5.3 eV to ~5.1 eV) and simultaneously enhanced the LUMO energy levels (~2.6 eV to ~2.9 eV). The introduction of an electron withdrawing group (**10a/b**) significantly enhanced the LUMO energy levels (~0.3 eV).



Scheme 4.



Scheme 2.



Scheme 3.

In summary, the synthesis of various benzo[*c*]thiophene analogs incorporating 9,9-dialkylfluorenyl units was achieved in reasonable yields. The highly soluble nature of these annelated thiophenes may make them suitable for transistor applications through spin-coating techniques. The higher-lying HOMO energy levels of these fluorene-incorporated benzo[*c*]heterocycles (~5.2 eV) greatly reduce the energy barrier for hole injection from ITO (φ = 4.8 eV) to emissive Alq_3 (φ = 4.8 eV), hence, these heterocycles should be explored as hole-transporting materials for double-layer OLEDs.

Table 2
Summary of the physical properties of selected benzo[*c*]thiophenes/benzo[*c*]selenophenes

Compound	λ_{max}[a] (nm)	λ_{onset} (nm)	λ_{emiss}[b] (nm)	E_g[c] (eV)	E_{ox}^{onset} (eV)	HOMO[d] (eV)	LUMO[e] (eV)
7i	445	475	539	2.61	0.82	5.26	2.65
7j	425	450	512	2.75	0.91	5.35	2.60
7k	430	455	515	2.72	0.85	5.29	2.57
8a	465	490	553	2.53	0.72	5.16	2.63
8b	440	470	541	2.64	0.76	5.20	2.56
8c	435	465	545	2.66	0.77	5.21	2.55
9a	495	550	597	2.25	0.67	5.11	2.86
9b	480	540	592	2.30	0.71	5.15	2.85
10a	510	570	605	2.17	0.69	5.13	2.96
10b	500	555	600	2.23	0.72	5.16	2.93

[a] Measured in dilute dichloromethane solution.
[b] Excited at the absorption maxima.
[c] Estimated from the onset of absorption ($E_g = 1240/\lambda_{onset}$).
[d] Calculated using the empirical equation: HOMO = $(4.44 + E_{ox}^{onset})$.
[e] Calculated from LUMO = HOMO − E_g.

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9. The required 9,9-dialkylfluorenes **2a/2b** were prepared from fluorene via successive lithiations using *n*-BuLi/THF at −78 °C, followed by quenching with alkyl halides.
10. The required aryl/hetero-aryl Grignard reagents were prepared from the corresponding bromo compounds by refluxing with magnesium in dry THF under a N_2 atmosphere.
11. *Spectral data of selected benzo[c]thiophenes*:Compound **7a**: mp 56 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.40 (t, *J* = 3.6 Hz, 6H), 2.06–2.15 (m, 4H), 7.01 (m, 1H), 7.14 (t, *J* = 3 Hz, 1H), 7.29–7.36 (m, 5H), 7.53 (d, *J* = 3 Hz, 1H), 7.7–7.92 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 32.9, 56.3, 118.9, 119.7, 120.1, 120.2, 120.3, 121.8, 122.2, 122.9, 123.8, 123.9, 125.2, 125.4, 125.6, 127.1, 127.2, 127.9, 130.2, 133.7, 140.1, 140.6, 141.1, 144.2, 150.2, and 150.7. Anal. Calcd for $C_{29}H_{24}S_2$: C, 79.77; H, 5.54; S, 14.69. Found: C, 79.60; H, 5.62; S, 14.78.

    Compound **7c**: viscous orange liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.41 (t, *J* = 7.35 Hz, 6H), 0.79–0.83 (m, 3H), 1.21–1.25 (m, 6H), 1.55-1.63 (m, 2H), 2.08 (q, *J* = 7.4 Hz, 4H), 2.67 (t, *J* = 8.25 Hz, 2H), 7.06–7.11 (m, 3H), 7.29–7.34 (m, 1H), 7.35–7.38 (m, 4H), 7.57–7.60 (m, 1H), 7.64–7.68 (m, 2H), 7.73–7.74 (m, 1H), 7.82–7.85 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 14.1, 22.6, 29, 29.1, 30.8, 31.6, 32.8, 56.3, 119.8, 120.2, 121.0, 121.8, 123.0, 123.7, 124.0, 124.2, 125.9, 127.0, 127.3, 128.1, 128.2, 129.3, 132.8, 134.3, 136.2, 138.0, 139.2, 141, 141.1, 142.3, 150.2, and 150.8. Anal. Calcd for $C_{35}H_{36}S_2$: C, 80.72; H, 6.97; S, 12.31. Found: C, 80.84; H, 7.05; S, 12.11.

    Compound **7i**: viscous orange liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79–0.89 (m, 10H), 10.8–1.24 (m, 12H), 2.10–2.18 (m, 4H), 7.10–7.22 (m, 3H), 7.36–7.47 (m, 4H), 7.61–7.62 (m, 1H), 7.80–7.88 (m, 3H), 7.92–8.02 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.7, 23.9, 29.8, 31.6, 40.5, 55.3, 119, 119.8, 120.1, 120.3, 120.4, 121.9, 122.2, 122.9, 123.9, 124.0, 125.3, 125.4, 125.5, 127.0, 127.2, 127.9, 130.3, 133.8, 140.1, 140.3, 140.8, 144.3, 151.1, and 151.6. Anal. Calcd for $C_{37}H_{40}S_2$: C, 80.97; H, 7.35; S, 11.68. Found: C, 80.85; H, 7.30; S, 11.85.

    Compound **7o**: viscous yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.62–0.65 (m, 10H), 0.89–1.11 (m, 12H), 1.80–1.83 (m, 4H), 3.71 (s, 3H), 6.95–6.98 (m, 4H), 7.20–7.24 (m, 3H), 7.49–7.73 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.8, 29.7, 31.5, 40.5, 55.2, 55.3, 114.6, 118.8, 119.7, 119.8, 120.2, 120.3, 121.3, 122.0, 122.9, 123.6, 124.7, 124.8, 125.1, 126.3, 126.9, 127.0, 130.4, 130.6, 139.8, 140.8, 143.9, 151.0, 151.5, and 158.8. Anal. Calcd for $C_{40}H_{44}S_2$: C, 83.87; H, 7.74; S, 5.60. Found: C, 83.80; H, 7.79; S, 5.65.
12. Mohanakrishnan, A. K.; Amaladass, P. *Tetrahedron Lett.* **2005**, *46*, 7201–7204.
13. *Spectral data for* **8b**: viscous yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81–0.90 (m, 13H), 1.15–1.32 (m, 18H), 1.61–1.68 (m, 2H), 2.05–2.10 (m, 4H), 2.71 (t, *J* = 7.8 Hz, 2H), 7.00–7.04 (m, 2H), 7.12 (d, *J* = 5.4 Hz, 1H), 7.37–7.48 (m, 5H), 7.63–7.66 (m, 2H), 7.74–7.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.1, 22.6, 23.9, 29.0, 29.1, 29.7, 30.8, 31.5, 31.6, 40.4, 55.2, 119.9, 120.2, 121.6, 122.4, 123.0, 123.7, 123. 8, 124.0, 125.9, 126.9, 127.3, 128.7, 129.2, 130.6, 132.8, 134.8, 136.6, 140.6, 140.8, 142.0, 146.1, 151.1, and 151.5. Anal. Calcd for $C_{43}H_{52}SSe$: C, 75.96; H, 7.71; S, 4.72. Found: C, 76.10; H, 7.70; S, 4.65.
14. *A representative procedure for the synthesis of 9a: A solution of* **7a** (0.4 g, 0.92 mmol) in dry CH_2Cl_2 was treated with $FeCl_3$ (0.30 g, 1.85 mmol) under a N_2 atmosphere at room temperature for 6 h. The reaction mixture was treated with a dilute solution of $N_2H_4{\cdot}H_2O$. Evaporation of the solvent followed by column chromatography (silica gel, hexane–EtOAc; 10:1) gave the dimer **9a** (0.18 g, 45%).

    Spectral data for **9a**: semi-solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.35 (t, *J* = 7.4 Hz. 12H), 2.0 (q, *J* = 7.4 Hz, 8H), 6.86–6.89 (m, 4H), 7.0–7.3 (m, 14H), 7.5 (m, 2H), 7.61–7.8 (m, 4H), 7.98 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 32.8, 56.3, 119.9, 120.2, 121.7, 123.0, 123.7, 124.3, 124.5, 124.9, 125.8, 126.1, 126.3, 126.9, 127.0, 127.4, 128.2, 132.5, 135.2, 135.3, 135.4, 136.6, 140.9, 141.3, 150.2, and 150.9. Anal. Calcd for $C_{58}H_{46}S_4$: C, 79.96; H, 5.32; S, 14.72. Found: C, 80.05; H, 5.35; S, 14.60.
15. *Spectral data for aldehyde* **10b**: red liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81–0.95 (m, 10H), 1.15–1.31 (m, 12H), 2.17–2.22 (m, 4H), 7.29–7.37 (m, 3H), 7.41 (d, *J* = 3.9 Hz, 1H), 7.61–7.66 (m, 5H), 7.67–7.81 (m, 3H), 7.81 (d, *J* = 8.3 Hz, 1H), 9.61 (s, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.7, 23.1, 29.5, 31.9, 40.7, 55.1, 119.1, 120.7, 121.4, 121.5, 123.1, 123.9, 124.7, 125.1, 126.9, 127.7, 128.5, 132.1, 133.9, 135.5, 136.1, 137.7, 138.5, 140.5, 141.5, 141.7, 147.1, 150.7, and 181.7.

    Spectral data for cyanovinylene **11b**: black solid; mp 117 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78–0.84 (m, 10H), 1.18–1.20 (m, 12H), 2.01–2.12 (m, 4H), 7.1 (t, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 8.7 Hz, 1H), 7.33–7.43 (m, 4H), 7.51–7.55 (m, 2H), 7.59–7.66 (m, 4H), 7.73–7.81 (m, 1H), 7.81–7.90 (m, 3H), 8.49–8.52 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 23.9, 29.8, 31.5, 40.5, 55.3, 119.0, 119.7, 120.2, 120.3, 120.5, 121.5, 122.9, 123.7, 124.2, 124.8, 125.3, 125.5, 125.8, 126.2, 126.3, 126.6, 126.9, 127.1, 127.4, 127.9, 128.6, 128.7, 130.6, 131.1, 134.4, 140.2, 140.8, 144.2, 145.6, 151.1, and 151.6. Anal. Calcd for $C_{44}H_{43}NS_3$: C, 77.49; H, 6.35; N, 2.05; S, 14.10. Found: C, 77.35; H, 6.31; N, 2.15; S, 14.18.