JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2003; **16:** 207–212
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.599

Synthesis and UV/Vis spectroscopic properties of new [2-(*N,N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates

Mihail Lucian Birsa[1]* and Dumitru Ganju[2]

[1]Department of Organic Chemistry, Faculty of Chemistry, 'Al.I. Cuza' University of Iasi, 11 Bd. Carol I, 6600 Iasi-6, Romania
[2]Department of Inorganic Chemistry, Faculty of Chemistry, 'Al.I. Cuza' University of Iasi, 11 Bd. Carol I, 6600 Iasi-6, Romania

Received 13 May 2002; revised 18 November 2002; accepted 5 December 2002

ABSTRACT: In weak alkaline aqueous medium, 4-(hydroxyphenyl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts led to the corresponding dipolar betaines. These compounds were described as zwitterionic phenolates with an intramolecular charge-transfer UV/Vis absorption and represent useful precursors for the preparation of the first 1,3-dithiolium chlorides. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: 1,3-dithiolium salts; mesoionic compounds; zwitterions; solvatochromism

INTRODUCTION

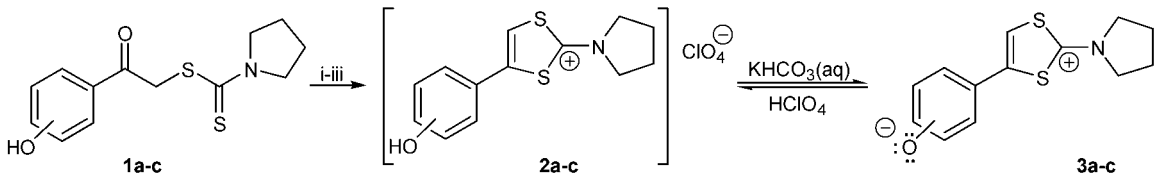
Compounds that exhibit intramolecular charge-transfer UV/Vis absorptions are of interest as chromophores for dyes, non-linear optics, synthetic light-harvesting systems and theoretical aspects of charge transport at the molecular level.[1–3] There is special interest in systems where the electron-donor moiety is linked through a π- or σ-bonded bridge to the electron-acceptor moiety.[4] Although tetrathiafulvalenes are well-known π-electron-donor systems, a variety of acceptor units have been investigated in this context. Special attention has been devoted to cationic systems such as pyridinium and bipyridium cations.[5–7] The charge-transfer properties of linked phenothiazine–bipyridinium systems have also been investigated.[8–12] In this context, it is presumed that 1,3-dithiolium ions can also serve as acceptor moieties in zwitterionic compounds with intramolecular charge-transfer absorptions. It should be noted that 1,3-dithiolium ions are also useful precursors for the synthesis of symmetrical and non-symmetrical tetrathiafulvalenes.[13–15] The synthesis of some 4-(3′,5′-dichloro-2′-hydroxyphenyl)-2-(*N,N*-dialkylamino)-1,3-dithiolium perchlorates by the Vilsmeier–Haack reagent, under Harnisch reaction conditions, on the corresponding *N,N*-dialkylaminocarbodithioates has been reported by Cascaval.[16] Instead of the expected 1,3-dithiols, the sodium tetrahydroborate reduction products of these 1,3-dithiolium salts have been proved to be 4,6-dichloro-2-[2-(*N,N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates, a new class of mesoionic compounds named by the author 'iasinone.' Although the failure of the reduction reactions is not clear, it is obvious that the basic conditions induced by sodium tetrahydroborate are responsible for the formation of dehydrohalogenated compounds. This unexpected result prompted us to undertake a study of the behaviour of 4-(2′-, 3′- and 4′-hydroxyphenyl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts in weak alkaline median, such as aqueous alkali metal hydrogencarbonates, and to investigate the π-acceptor properties of the 1,3-dithiolium ion unit.

**Correspondence to:* M. L. Birsa, Department of Organic Chemistry, Faculty of Chemistry, 'Al.I. Cuza' University of Iasi, 11 Bd. Carol I, 6600 Iasi-6, Romania.
E-mail: lbirsa@uaic.ro

RESULTS AND DISCUSSION

4-(2′-Hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2a**) and 4-(4′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2b**) were synthesized as colourless crystals by cyclization of 1-(hydroxyphenyl)-2-(pyrrolidin-1-ylthiocarbonylthio)-1-ethanones (**1a** and **1b**), in the presence of H_2SO_4–CH_3CO_2H (1:3, v/v), followed by addition of 70% perchloric acid to the reaction medium (Scheme 1) (for other variants, see Ref. 17). The latter are easily available from reaction of the corresponding hydroxyphenacyl halides and pyrrolidinium pyrrolidin-1-ylcarbodithioate. Treatment of perchlorates **2a** and **2b**, under heterogeneous conditions, with saturated aqueous potassium hydrogencarbonate solution affords [2-(pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolates (**3a** and **3b**), in quantitative yields. The molecular structure of the new compounds was proved by analytical and spectral data and by the following chemical transformation: treatment of an acetone suspension of the zwitterionic compounds **3a** and **3b** with 70%

Copyright © 2003 John Wiley & Sons, Ltd.



Scheme 1. (i) H_2SO_4–CH_3CO_2H (1:3, v/v), 60 °C; (ii) 70% $HClO_4$; (iii) H_2O.

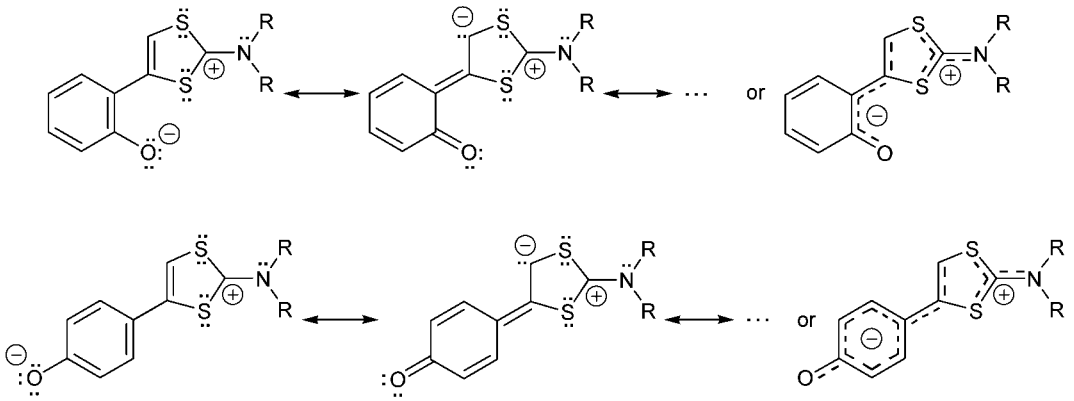
Entry	OH position	Product	Yield (%)
1a	2′	**2a**	97
1b	4′	**2b**	98
1c	3′	**2c**	86
2a	2′	**3a**	100
2b	4′	**3b**	100
2c	3′	**3c**	100

perchloric acid regenerates the 1,3-dithiolium perchlorates **2a** and **2b** in quantitative yields (Scheme 1).

2- and 4-[2-(pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolates were isolated as yellow crystalline products that present the features of mesoionic compounds (Scheme 2).[18–20] The presence of a hydroxy substituent in an *ortho*- or *para*-position induces an extended delocalization of the negative charge up to the C-4—C-5 bond of the dithiolium ring.

In order to investigate if the yellow colour of these mesoionic compounds is due to the contribution of the quinonoid structure of the electronic ground state, 4-(3′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate was synthesized, as above (Scheme 1). Treatment of this perchlorate with saturated potassium hydrogencarbonate solution afforded 3-[2-(pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolate (**3c**) whose colour also is yellow. Compound **3c**, for which the extended quinonoide conjugation is inoperative, must be written only as simple zwitterionic compound. This shows that the yellow colour of 2-, 3-, and 4-[2-(*N,N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates is not due to the contribution of the quinonoide structure to the ground state. A comparative study of the UV/Vis spectra (in methanol) of the zwitterionic phenolates **3a–c** confirms the above conclusion. In these spectra, the extinction coefficients of the peaks at $\lambda_{max} = 375$ nm are identical for all phenolates ($\log \epsilon \approx 3.4$) (Fig. 1). In the case of **3c**, a hypsochromic effect for the $n \rightarrow \pi^*$ transition may be observed ($\lambda = 310$ nm vs 315 nm in the case of **3a**), because the delocalization of the negative charge is operative only on the benzene ring. These facts suggest that the yellow colour of these zwitterionic phenolates is due to a charge transfer between electron-rich and electron-deficient regions of the molecule.[21,22]

The intramolecular nature of the charge-transfer band was proved by measurements at different concentrations. Usually, the intramolecular charge-transfer UV/Vis absorption of such zwitterionic chromophores results from a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part. For this reason, the position of the charge-transfer band should depend on



Scheme 2

Copyright © 2003 John Wiley & Sons, Ltd.

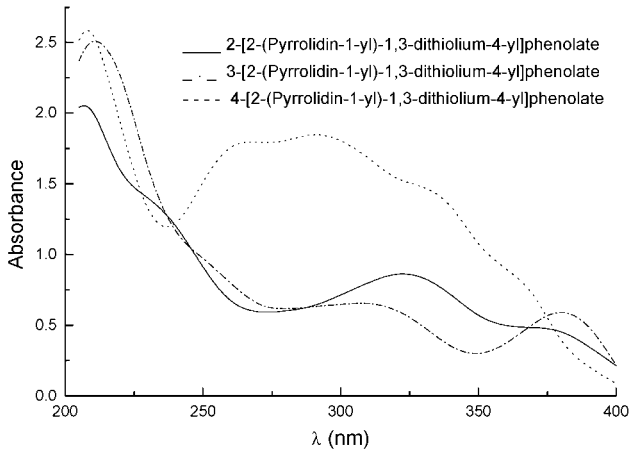


Figure 1. UV/Vis absorption spectra of the zwitterionic phenolates **3a–c** (in methanol)

solvent polarity,[23–27] defined here as the overall solvation capability of a solvent (for definitions of the term solvent polarity, see Refs 26 and 27). Therefore, we decided to investigate the solvatochromism of the zwitterionic compounds **3a–c**. From the $E_T(30)$ solvent polarity scale,[5,23,28–31] methanol was found as the highest polarity solvent, which ensures a sufficient concentration for UV/Vis measurements. In acetonitrile, a solvent of intermediate polarity, the UV/Vis spectra of **3a–c** look similar to those in methanol. Only the position of the long-wavelength absorption band is slightly solvent dependent; the others are not. Even in 1,4-dioxane, a low-polarity solvent, the bathochromic charge-transfer band shift is small ($\Delta\lambda = 10$–20 nm, see Table 1). The highest shift ($\Delta\lambda = 20$ nm) was recorded in the case of 3-[2-(pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolate (**3c**). Thus, with increasing solvent polarity, a hypsochromic band shift of $\Delta\lambda = -10$ to -20 nm for **3a–c** is observed, corresponding to a negative solvatochromism. These results appear to be the result of a decrease in the ionization energy of the phenolate moiety because of delocalization of the negative charge in the case of mesoionic compounds **3a** and **3b** up to the C-5 atom of the dithiolium ring (see Scheme 2). On going from mesoionic compound **3a** to **3b** and to zwitterionic derivative **3c**, the electronic density at C-5 decreases significantly, with the experimentally observed hypsochromic charge-transfer band shift with increasing solvent polarity as a consequence.

Table 1. Long-wavelength, solvent-dependent charge-transfer absorption maxima, λ_{max} (nm), of zwitterionic phenolates **3a–c**, measured at 25 °C and at normal pressure

Solvent	3a	3b	3c
Methanol	375	375	375
Acetonitrile	378	378	379
N,N-Dimethylformamide	380	381	384
Tetrahydrofuran	382	384	389
1,4-Dioxane	385	390	395
$\Delta\lambda$ (nm)	−10	−15	−20

On protonation of the phenolate parts of **3a–c** the charge-transfer bands disappear and the corresponding 1,3-dithiolium salts formed absorb at $\lambda_{max} = 325$ nm. It should be noted that the absorption spectra of 4-hydroxyphenyl-2-(*N,N*-dialkylamino)-1,3-dithiolium salts exhibit broad analogies with those of 4-phenyl-2-(*N,N*-dialkylamino)-1,3-dithiolium salts.[32] Despite the colour changes during the protonation–deprotonation reactions, the use of these new compounds as pH indicators appears to be limited to those systems which allow the presence of suitable organic solvents such as *N,N*-dimethylformamide.

It is well known that 1,3-dithiolium chlorides cannot be isolated from the reaction media; only di(1,3-benzodithiolium) tetrachlorozincate has been isolated so far.[33] However, we have been able to isolate the first 1,3-dithiolium chloride using the interconversion possibilities between the mesoionic phenolate and its salts. Thus, 4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride was isolated as a solid crystalline product by the treatment of an acetonic suspension of **3a** with 37% hydrochloric acid. As expected, this compound is sufficiently soluble in water to allow the measurement of the UV spectra in this solvent. The above conclusions are supported by the UV/Vis absorption spectrum of 4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride. We expected a hypsochromic band shift because of the increase in polarity of the solvent, but the results exceeded all expectations. By comparison with the electronic spectra of the 4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride in methanol, a very strong hypsochromic effect was recorded for all absorption bands ($\Delta\lambda \approx 70$ nm) (Fig. 2). Moreover, a new absorption band appeared at $\lambda_{max} = 375$ nm ($\log \epsilon = 2.3$). The presence of this peak suggests that in water the

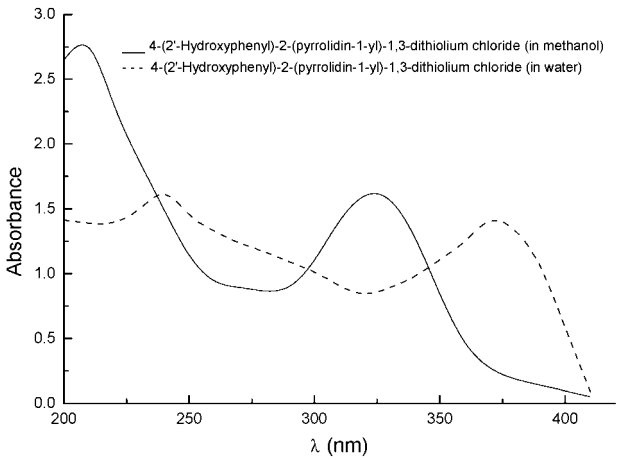


Figure 2. UV/Vis absorption spectra of the 4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride in water and methanol

Copyright © 2003 John Wiley & Sons, Ltd.

4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride exists in equilibrium with the corresponding mesoionic phenolate **3a**. The fact that the solvent polarity does not have a great influence on the position of this absorption band is supplementary confirmation of the internal charge-transfer character of the long-wavelength absorption bands of 2−, 3−and 4-[2-(*N,N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates.

In summary, this work demonstrates the internal charge-transfer character of the long-wavelength absorption bands of 2−, 3−and 4-[2-(*N,N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates. These compounds exhibit a small negative solvatochromism and are useful precursors for the first 1,3-dithiolium chloride as a solid crystalline product. The extension of these studies to other substrates is under way.

EXPERIMENTAL

Melting-points were obtained on a Mel-Temp II apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are reported in ppm downfield from TMS. ^{13}C NMR assignments according with DEPT experiments are given as follows: +, for CH and CH_3 carbon atoms, −, for CH_2 carbon atoms, ×, for quarternary carbons. IR spectra were recorded on a Digilab FTS-40 spectrometer in KBr pellets. Mass spectra were recorded on a Finnigan GC/MS 4021 spectrometer. UV/Vis absorption spectra were recorded on a Cecil 1020 spectrophotometer.

*1-(2′-Hydroxyphenyl)-2-(pyrrolidin-1-ylthiocarbonylthio)-1-ethanone (**1a**). Typical procedure.* To a solution of 2-chloro-1-(2′-hydroxyphenyl)-1-ethanone[34] (1.7 g, 10 mmol) in acetone (30 ml), a solution of pyrrolidinium pyrrolidin-1-ylcarbodithioate (2.18 g, 10 mmol) in acetone–water (15 ml + 15 ml) was added. The reaction mixture was heated under reflux for 10 min, then cooled and poured into water (200 ml). The resulting precipitate was filtered off, washed with water and dried. Recrystallization from EtOH (50 ml) gave the pure product as pale yellow crystals, yield 2.61 g (93%), m.p. 148–149 °C. ^{1}H NMR ($CDCl_3$), δ: 1.98 (m, 2H), 2.10 (m, 2H), 3.74 (t, 2H, J = 6.4 Hz), 3.91 (t, 2H, J = 6.4 Hz), 4.95 (s, 2H), 6.94 (ddd, 1H, J = 8.1, 8.1 and 1.1 Hz), 6.98 (dd, 1H, J = 7.8 and 1.1 Hz), 7.50 (ddd, 1H, J = 8.1, 7.8 and 1.6 Hz), 7.98 (dd, 1H, J = 8.1 and 1.6 Hz), 11.85 (s, OH). ^{13}C NMR ($CDCl_3$), δ: 24.35 (−), 26.16 (−), 43.77 (−), 50.83 (−), 55.64 (−), 118.56 (+), 118.92 (×), 119.28 (+), 130.30 (+), 136.92 (+), 162.41 (×), 190.45 (×), 199.02 (×). IR (KBr): 2975, 2860, 1634, 1470, 1358, 1265, 1210, 1050, 868, 762 cm^{-1}. MS (EI): *m/z* (%) 281 [M^+] (15), 248 (36), 146 (18), 121 (16), 114 (100). Anal. Calcd for $C_{13}H_{15}NO_2S_2$ (**1a**): C, 55.49; H, 5.37; N, 4.98; S, 22.79. Found: C, 55.40; H, 5.33; N, 5.05; S, 22.53%.

*1-(4′-Hydroxyphenyl)-2-(pyrrolidin-1-ylthiocarbonylthio)-1-ethanone (**1b**).* This was prepared from 2-bromo-1-(4′-hydroxyphenyl)-1-ethanone;[35] yield 86%, m.p. 193–194 °C (decomp.). ^{1}H NMR (acetone-d_6), δ: 1.99 (m, 2H), 2.12 (m, 2H), 3.73 (t, 2H, J = 6.3 Hz), 3.92 (t, 2H, J = 6.3 Hz), 4.80 (s, 2H), 6.88 (d, 2H, J = 8.8 Hz), 7.94 (d, 2H, J = 8.8 Hz), 9.12 (s, OH). ^{13}C NMR (acetone-d_6), δ: 24.82 (−), 26.53 (−), 44.00 (−), 50.23 (−), 54.34 (−), 114.90 (+), 127.84 (×), 130.48 (+), 161.60 (×), 190.98 (×), 193.56 (×). IR (KBr): 3226, 2977, 1663, 1585, 1422, 1276, 1180, 984, 829, 606 cm^{-1}. MS (EI): *m/z* (%) 281 [M^+] (24), 248 (46), 146 (20), 121 (15), 114 (100). Anal. Calcd for $C_{13}H_{15}NO_2S_2$ (**1b**): C, 55.49; H, 5.37; N, 4.98; S, 22.79. Found: C, 55.44; H, 5.30; N, 5.15; S, 22.63%.

*1-(3′-Hydroxyphenyl)-2-(pyrrolidin-1-ylthiocarbonylthio)-1-ethanone (**1c**).* This was prepared from 2-bromo-1-(3′-hydroxyphenyl)-1-ethanone;[35] yield 76%, m.p. 165–166 °C. ^{1}H NMR (DMSO-d_6), δ: 2.16 (m, 4H), 3.99 (t, 2H, J = 6.2 Hz), 4.20 (t, 2H, J = 6.2 Hz), 5.39 (s, 2H), 7.55 (ddd, 1H, J = 8.0, 1.0 and 1.0 Hz), 7.81 (dd, 1H, J = 8.0 and 7.8 Hz), 7.92 (dd, 1H, J = 1.0 and 1.0 Hz), 7.98 (ddd, 1H, J = 7.8, 1.0 and 1.0 Hz), 10.20 (s, OH). ^{13}C NMR (DMSO-d_6), δ: 24.45 (−), 26.30 (−), 44.85 (−), 51.89 (−), 53.54 (−), 115.29 (+), 119.82 (+), 121.18 (+), 130.42 (+), 138.54 (×), 158.70 (×), 193.33 (×), 194.21 (×). IR (KBr): 3355, 2934, 1663, 1585, 1482, 1439, 1327, 1233, 994, 758 cm^{-1}. MS (EI): *m/z* (%) 281 [M^+] (52), 248 (33), 146 (16), 114 (100). Anal. Calcd for $C_{13}H_{15}NO_2S_2$ (**1c**): C, 55.49; H, 5.37; N, 4.98; S, 22.79. Found: C, 55.34; H, 5.22; N, 4.72; S, 22.69%.

*4-(2′-Hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2a**). Typical procedure.* To a mixture of H_2SO_4 (98%, 1.4 ml) and glacial AcOH (4.2 ml), 1-(2′-hydroxyphenyl)-2-(pyrrolidin-1-ylthiocarbonylthio)-1-ethanone (**1a**) (1.4 g, 5 mmol) was added in few portions at room temperature. The reaction mixture was warmed at 80 °C for 10 min and then $HClO_4$ (70%, 0.7 ml) was added. The crude reaction product was precipitated with water (150 ml), filtered off and dried. Recrystallization from EtOH (40 ml) gave the pure product as colourless crystals; yield 1.76 g (97%), m.p. 210–211 °C. ^{1}H NMR (DMSO-d_6), δ: 2.19 (m, 4H), 3.73 (m, 4H), 6.98 (ddd, 1H, J = 7.1, 7.1 and 1.1 Hz), 7.02 (dd, 1H, J = 7.9 and 1.1 Hz), 7.33 (ddd, 1H, J = 7.9, 7.1 and 1.6 Hz), 7.59 (dd, 1H, J = 7.1 and 1.6 Hz), 7.97 (s, 1H), 11.24 (s, OH). ^{13}C NMR (DMSO-d_6), δ: 26.45 (−), 26.65 (−), 56.86 (−), 57.22 (−), 116.89 (+), 117.47 (×), 119.51 (+), 120.63 (+), 128.93 (+), 132.08 (+), 135.81 (×), 154.16 (×), 182.10 (×). IR (KBr): 3372, 3097, 1559, 1516, 1456, 1259, 1104 (b), 778 cm^{-1}. MS (CI, NH_3): *m/z* (%) 281 [MNH_3^+-ClO_4] (40), 248 (73), 193 (33), 181 (100), 159 (62), 145 (69), 120 (70). Anal. Calcd for $C_{13}H_{14}ClNO_5S_2$ (**2a**): C, 42.91; H, 3.88; Cl, 9.74; N, 3.85; S, 17.63. Found: C, 42.75; H, 3.81; Cl, 9.85; N, 3.70; S, 17.42%.

Copyright © 2003 John Wiley & Sons, Ltd.

*4-(4′-Hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2b**).* Yield 98%, m.p. 258–259 °C (decomp.) (colourless crystals). ^{1}H NMR (DMSO-d_6), δ: 2.32 (m, 4H), 3.82 (t, 2H, J = 6.9 Hz), 3.86 (t, 2H, J = 6.9 Hz), 6.87 (d, 2H, J = 8.7 Hz), 7.48 (d, 2H, J = 8.7 Hz), 7.68 (s, 1H), 10.15 (s, OH). ^{13}C NMR (DMSO-d_6), δ: 26.53 (−), 26.59 (−), 55.24 (−), 56.18 (−), 115.32 (+), 116.74 (+), 121.11 (×), 128.82 (+), 139.15 (×), 159.83 (×), 185.99 (×). IR (KBr): 3261, 1607, 1572, 1506, 1448, 1280, 1115 (b), 836 cm^{-1}. MS (CI, NH_3): *m/z* (%) 281 [MNH_3^+-ClO_4] (33), 248 (65), 235 (24), 193 (31), 181 (100), 159 (55), 145 (65), 98 (62). Anal. Calcd for $C_{13}H_{14}ClNO_5S_2$ (**2b**): C, 42.91; H, 3.88; Cl, 9.74; N, 3.85; S, 17.63. Found: C, 42.99; H, 3.95; Cl, 9.66; N, 3.77; S, 17.49%.

*4-(3′-Hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2c**).* Yield 86%, m.p. 195–196 °C (colourless crystals). ^{1}H NMR (DMSO-d_6), δ: 2.07 (m, 4H), 3.79 (m, 4H), 6.91 (ddd, 1H, J = 7.8, 1.6 and 1.2 Hz), 6.99 (dd, 1H, J = 1.6 and 1.1 Hz), 7.05 (ddd, 1H, J = 7.6, 1.2 and 1.1 Hz), 7.32 (dd, 1H, J = 7.8 and 7.6 Hz), 7.87 (s, 1H), 9.97 (s, OH). ^{13}C NMR (DMSO-d_6), δ: 26.12 (−), 26.25 (−), 56.50 (−), 57.52 (−), 113.56 (+), 117.81 (+), 117.96 (+), 131.30 (+), 131.36 (+), 137.78 (×), 158.63 (×), 185.95 (×). IR (KBr): 3306, 1603, 1570, 1430, 1120 (b), 850 cm^{-1}. MS (CI, NH_3): *m/z* (%) = 281 [MNH_3^+–ClO_4] (53), 248 (44), 193 (40), 181 (100), 145 (50), 98 (61). Anal. Calcd for $C_{13}H_{14}ClNO_5S_2$ (**2c**): C, 42.91; H, 3.88; Cl, 9.74; N, 3.85; S, 17.63. Found: C, 42.85; H, 3.79; Cl, 9.63; N, 3.72; S, 17.39%.

*2-[2-(Pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolate (**3a**). Typical procedure.* To a saturated aqueous potassium hydrogencarbonate solution, 4-(2′-hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorate (**2a**) (0.36 g, 1 mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2 h with vigorous stirring at room temperature, the precipitate was filtered off, washed with water and dried. Recrystallization from DMF–AcOMe gave the pure product as yellow crystals; yield 0.26 g (100%), m.p. 218 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 2.21 (m, 4H), 3.75 (m, 4H), 6.96 (ddd, 1H, J = 7.0, 6.9 and 1.2 Hz), 7.02 (dd, 1H, J = 7.7 and 1.2 Hz), 7.34 (ddd, 1H, J = 7.7, 7.0 and 1.5 Hz), 7.72 (dd, 1H, J = 6.9 and 1.5 Hz), 7.99 (s, 1H). ^{13}C NMR (DMSO-d_6), δ: 26.49 (−), 26.71 (−), 56.92 (−), 57.20 (−), 116.94 (+), 117.50 (×), 119.33 (+), 120.44 (+), 128.88 (+), 132.07 (+), 135.91 (×), 154.43 (×), 182.17 (×). IR (KBr): 3386, 1541, 1503, 1432, 1020 (b), 840 cm^{-1}. MS (CI, NH_3): *m/z* (%) 264 [MH^+] (31), 231 (65), 189 (82), 114 (38), 71 (100). Anal. Calcd for $C_{13}H_{13}NOS_2$ (**3a**): C, 59.28; H, 4.98; N, 5.32; S, 24.35. Found: C, 59.05; H, 4.71; N, 5.15; S, 24.08%.

*4-[2-(Pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolate (**3b**).* Yield 100%, m.p. 129–130 °C (decomp.) (yellow crystals). ^{1}H NMR (DMSO-d_6), δ: 2.14 (m, 4H), 3.84 (m, 4H), 6.75 (d, 2H, J = 8.6 Hz), 7.38 (d, 2H, J = 8.6 Hz), 7.61 (s, 1H). ^{13}C NMR (DMSO-d_6), δ: 26.24 (−), 26.32 (−), 55.18 (−), 55.36 (−), 115.64 (+), 116.88 (+), 121.58 (×), 128.72 (+), 139.62 (×), 160.46 (×), 183.37 (×). IR (KBr): 3407, 1585, 1508, 1448, 1035, 838 cm^{-1}. MS (CI, NH_3): *m/z* (%) 264 [MH^+] (36), 231 (60), 189 (75), 114 (45), 71 (100). Anal. Calcd for $C_{13}H_{13}NOS_2$ (**3b**): C, 59.28; H, 4.98; N, 5.32; S, 24.35. Found: C, 59.36; H, 4.83; N, 5.19; S, 24.12%.

*3-[2-(Pyrrolidin-1-yl)-1,3-dithiolium-4-yl]phenolate (**3c**).* Yield 100%, m.p. 128–129 °C (yellow crystals). ^{1}H NMR (DMSO-d_6), δ: 2.11 (m, 4H), 3.58 (m, 4H), 6.81 (ddd, 1H, J = 7.7, 1.5 and 1.3 Hz), 6.87 (dd, 1H, J = 1.5 and 1.2 Hz), 6.95 (ddd, 1H, J = 7.5, 1.3 and 1.2 Hz), 7.22 (dd, 1H, J = 7.7 and 7.5 Hz), 7.82 (s, 1H). ^{13}C NMR (DMSO-d_6), δ: 25.85 (−), 26.94 (−), 55.87 (−), 55.96 (−), 113.79 (+), 116.79 (+), 117.67 (+), 125.44 (+), 130.97 (+), 136.54 (×), 158.87 (×), 184.32 (×). IR (KBr): 3415, 1580, 1498, 1453, 1029, 830 cm^{-1}. MS (CI, NH_3): *m/z* (%) 264 [MH^+] (49), 231 (55), 189 (81), 114 (32), 71 (100). Anal. Calcd for $C_{13}H_{13}NOS_2$ (**3c**): C, 59.28; H, 4.98; N, 5.32; S, 24.35. Found: C, 59.16; H, 4.79; N, 5.26; S, 24.09%.

4-(2′-Hydroxyphenyl)-2-(pyrrolidin-1-yl)-1,3-dithiolium chloride. To a suspension of **3a** (1 g, 3.8 mmol) in acetone (10 ml), HCl (37%, 1.6 ml, 19 mmol) was added. The reaction mixture was kept for 2 h with vigorous stirring at room temperature. The white solid was filtered, washed with acetone and dried. Recrystallization from EtOH (10 ml) gave pure 1,3-dithiolium chloride as colourless crystals; yield 1.1 g (98%), m.p. 208–209 °C. ^{1}H NMR (DMSO-d_6), δ: 2.28 (m, 4H), 3.73 (m, 4H), 6.82 (ddd, 1H, J = 7.1, 7.1 and 1.2 Hz), 6.98 (dd, 1H, J = 7.9 and 1.2 Hz), 7.47 (ddd, 1H, J = 7.9, 7.1 and 1.5 Hz), 7.84 (dd, 1H, J = 7.1 and 1.5 Hz), 8.05 (s, 1H), 11.54 (s, OH). ^{13}C NMR (DMSO-d_6), δ: 26.40 (−), 26.63 (−), 56.92 (−), 57.29 (−), 116.58 (+), 117.32 (×), 119.46 (+), 120.28 (+), 128.68 (+), 132.24 (+), 135.41 (×), 154.53 (×), 182.85 (×). IR (KBr): 3395, 3109, 1562, 1510, 1448, 1261, 1042, 732 cm^{-1}. MS (CI, NH_3): *m/z* (%) 264 [M^+ - Cl] (35), 248 (56), 193 (40), 181 (100), 145 (75), 120 (68). Anal. Calcd for $C_{13}H_{14}ClNOS_2$: C, 52.07; H, 4.71; Cl, 11.82; N, 4.67; S, 21.39. Found: C, 51.86; H, 4.65; Cl, 11.63; N, 4.53; S, 21.11%.

Acknowledgement

This paper is dedicated to Professor Dr Candiano Leonte on the occasion of his 70th birthday.

Copyright © 2003 John Wiley & Sons, Ltd.

REFERENCES

1. Paddon Row MN. *Acc. Chem. Res.* 1994; **27**: 18–25.
2. Imahori H, Sasaka Y. *Adv. Mater.* 1997; **9**: 537–546.
3. Ashwell GJ. *J. Mater. Chem.* 1999; **9**: 1991–2003.
4. Bryce MR. *Adv. Mater.* 1999; **11**: 11–23.
5. Reichardt C. *Chem. Rev.* 1994; **94**: 2319–2358.
6. Goldenberg LM, Becker JY, Levi OP-T, Khodorkovsky VY, Shapiro LM, Bryce MR, Cresswell JP, Petty MC. *J. Mater. Chem.* 1997; **7**: 901–907.
7. Simonsen KB, Zong K, Rogers RD, Cava MP, Becher J. *J. Org. Chem.* 1997; **62**: 679–686.
8. Kawanishi Y, Kitamura N, Tazuke S. *J. Phys. Chem.* 1986; **90**: 2469–2475.
9. Kawanishi Y, Kitamura N, Tazuke S. *J. Phys. Chem.* 1986; **90**: 6034–6037.
10. Yonemura H, Nakamura H, Matsuo T. *Chem. Phys.* 1992; **162**: 69–78.
11. Petry C, Lang M, Staab HA, Bauer H. *Angew. Chem.* 1993; **105**: 1791–1795; *Angew. Chem., Int. Ed. Engl.* 1993; **32**: 1711–1714.
12. Bauer H, Stier F, Petry C, Knorr A, Stadler C, Staab HA. *Eur. J. Org. Chem.* 2001; 1711–1714.
13. Narita M, Pittman CU Jr. *Synthesis* 1976; 489–514.
14. Schukat G, Richter AM, Fanghänel E. *Sulfur Rep.* 1987; **7**: 155–240.
15. Schukat G, Fanghänel E. *Sulfur Rep.* 1993; **14**: 245–390.
16. Cascaval A. *Mem. Sect. Stiint.-Acad. Rom.* 1984 (Pub. 1986); **7**: 87–108; *Chem. Abstr.* 1987; **107**: 96516.
17. (a) Leaver D, Robertson WAH, McKinnon DM. *J. Chem. Soc.* 1962; 5104–5109; (b) Campaigne E, Jacobsen NW. *J. Org. Chem.* 1962; **29**: 1703–1708; (c) Takamizawa A, Hirai K. *Chem. Pharm. Bull.* 1969; **17**: 1924–1930.
18. Miller J, Oliveira MB, Pereira AB, Galembeck SE, Moura GLC, Simas AM. *Phosphorus Sulfur Silicon Relat. Elem.* 1996; **108**: 75–84.
19. Simas AM, Miller J, Athayde Filho PF. *Can. J. Chem.* 1998; **76**: 869–872.
20. Athayde Filho PF, Miller J, Simas AM. *Synthesis* 2000; 1565–1568.
21. Mulliken RS. *J. Phys. Chem.* 1952; **56**: 801–822.
22. Mulliken RS. *J. Am. Chem. Soc.* 1952; **74**: 811–824.
23. Dimroth K, Reichardt C, Siepmann Th, Bohlmann F. *Justus Liebigs Ann. Chem.* 1963; **661**: 1–37.
24. Reichardt C, Schäfer G. *Liebigs Ann. Chem.* 1995; 1579–1582.
25. Reichardt C. *Chem. Soc. Rev.* 1992; **21**: 147–153.
26. Müller P. *Pure Appl. Chem.* 1994; **66**: 1077–1184 (particularly p. 1151).
27. Reichardt C. *Nachr. Chem. Tech. Lab.* 1997; **45**: 759–763.
28. Reichardt C, Harbusch-Görnert E. *Liebigs Ann. Chem.* 1983; 751–743.
29. Reichardt C. *Solvents and Solvent Effects in Organic Chemistry* (2nd edn). VCH: Weinheim, 1988; chapt. 7, 339–405.
30. Reichardt C, Che D, Heckenkemper G, Schäfer G. *Eur. J. Org. Chem.* 2001; 2343–2361.
31. Reichardt C, Eschner M, Schäfer G. *J. Phys. Org. Chem.* 2001; **14**: 737–751.
32. Takamizawa A, Hirai K. *Chem. Pharm. Bull.* 1969; **17**: 1924.
33. Nakayama J, Fujiwara K, Hoshino M. *Bull. Chem. Soc. Jpn.* 1976; **49**: 3567–3573.
34. Fries K, Pfaffendorf W. *Ber. Dtsch. Chem. Ges.* 1910; **43**: 212–219.
35. Pasaribu SJ, Williams LR. *Aust. J. Chem.* 1973; **26**: 1327–1331.

Copyright © 2003 John Wiley & Sons, Ltd.