Preparation and Spectroscopic Characterisation of Some 5-Methylmercapto- and 5-Dimethylamino-substituted Tris-(2-thienyl)methinium Perchlorates

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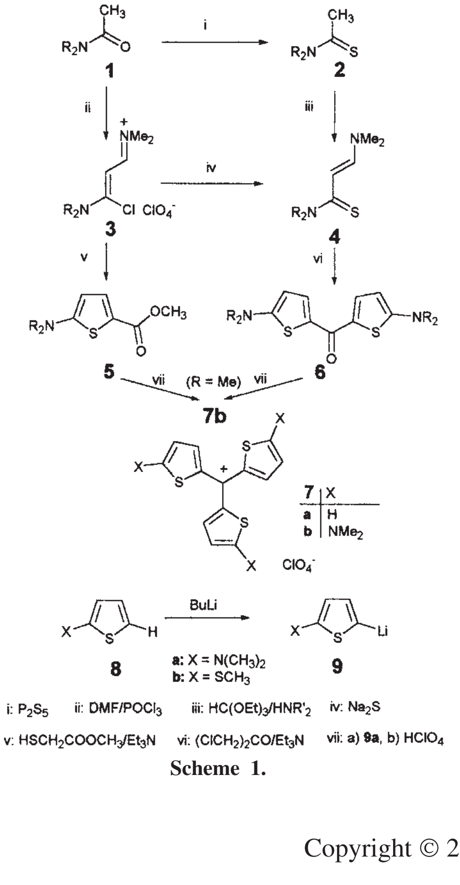
A series of deeply coloured 5-methylmercapto and 5-dimethylamino substituted tris(2-thienyl)methinium perchlorates has been prepared by the reaction of 2-methylmercapto-5-lithiothiophene with methyl 2-dimetylamino-5-thiophenecarboxylate, bis(2-dimethylamino)ketone, or diethyl carbonate, respectively. The products have been characterized spectroscopically.

Similar to their carbocyclic aniline derivatives the *N*-disubstituted alkyl 2-aminothiophene carboxylates **5**[1] and bis(2-aminothienyl)ketones **6**[2] are versatile starting materials for preparing dyes derived from the strongly electron-donating 2-amino-thiophene moiety. For instance, the alkyl 2-aminothiophene carboxylates **5** can be used for the synthesis of deeply coloured and strongly solvatochromic thiophene azo dyes.[3] The bis(2-aminothienyl)ketones **6** have been used to synthesise new heterocyclic Crystal Violet analogous **7**.[4] These deeply coloured methine dyes have been prepared by reaction of *N*-disubstituted 2-aminothiophenes **8a** with the ketones **6** in presence of $POCl_3$. They can be alternatively prepared, as we found, by reaction of the lithium compound **9a** with dimethyl carbonate, the ketones **6**, or with methyl 2-aminothiophene carboxylates **5**.

In contrast to their carbocyclic benzene analogues the mentioned dye precursors **5** and **6** are readily available by a ring-closure reaction starting from simple acyclic compounds. Thus, by using *N*-disubstituted acetamides **1** or thioacetamides **2** the *N*,*N'*-persubstituted 1-chlorovinamidinium salts **3**[5] or the *N*,*N'*-disubstituted thioacrylamides **4**[6] are available and can be transformed into the mentioned products by reaction with alkyl thioglycolates[1] or 1,3-dichloropropanone.[2]

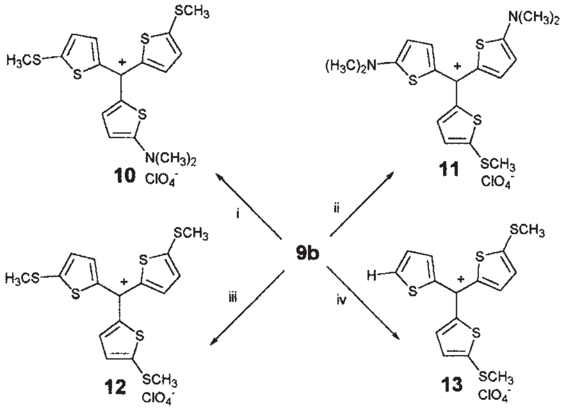


i: P_2S_5 ii: $DMF/POCl_3$ iii: $HC(OEt)_3/HNR'_2$ iv: Na_2S
v: $HSCH_2COOCH_3/Et_3N$ vi: $(ClCH_2)_2CO/Et_3N$ vii: a) **9a**, b) $HClO_4$

Scheme 1.

Now we describe the reaction of the compounds **5** and **6** ($R = CH_3$) with the lithiated species **9b** of 2-methylmercaptothiophene **8b**[7] giving rise to the formation of the methylmercapto-substituted tris(2-thienyl)methinium ions **10** and **11**. The reaction proceeds via intermediate carbinols which were transformed after their formation into corresponding perchlorates by subsequent addition of perchloric acid into the etheral solution.

To study the effect of methylmercapto as well as dimethylamino groups on the spectral properties of tris(2-thienyl)methinium ions we have additionally synthesized the tris(5-methylmercapto-2-thienyl)methinium perchlorate **12** and bis(5-methylmercapto-2-thienyl)2-thienylmethinium perchlorate **13** by reaction of three or two equivalents of the lithium compound **9b** with one equivalent of diethyl carbonate or methyl thiophene-2-carboxylate, resp., and subsequent addition of perchloric acid to the reaction mixture obtained.

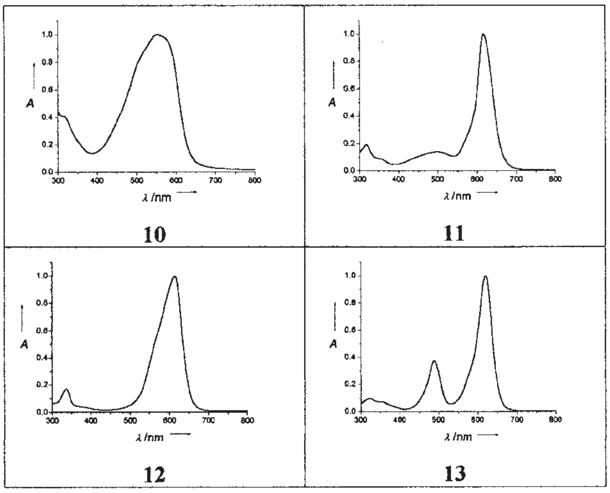


i: a) **5a**, b) $HClO_4$ ii: a) **6a**, b) $HClO_4$ iii: a) $(EtO)_2CO$ b) $HClO_4$
iv: a) $C_4H_3SCOOCH_3$ b) $HClO_4$

Scheme 2.

All new tris(2-thienyl)methinium perchlorates **7b** and **10**–**12** prepared are deeply coloured compounds which have been characterised by means of elemental analysis and NMR spectroscopic data.[8] Thus, these tris(2-thienyl)methinium perchlorates exhibit in their ^{1}H NMR spectra characteristic signals at about 3.00 and 7.00 ppm. Whereas the first signals can be attributed to the methyl groups on N or S the other ones occur as doublets and are assigned to the thienyl-bounded protons.

All dimethylamino and methylmercapto-substituted tris(2-thienyl)cations **7b** and **10**–**12** studied exhibit intense absorptions as shown by the absorption spectra (Figure 1) and spectral data



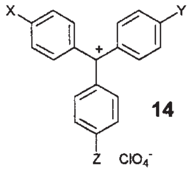
10 **11** **12** **13**

Figure 1. Absorption spectra of the tris-(2-thienyl)methinium perchlorates **10–13**.

(Table 1). Their maxima are found around 600 nm almost independently from the number of dimethylamino or methylmercapto groups. This fact is rather surprising since both groups differ significantly in their electron-donor properties judging from their Hammett σ_X-values.[9]

This is, however, in accordance with the spectral effect of both groups found at the carbocyclic dimethylamino- or methylmercapto-substituted triphenylmethinium derivatives **14**.[10,11] In this series both the dimethylamino as well as the methylmercapto group have nearly the same spectral effect on the longest-wavelength absorption maxima of the appropriate methinium ions (see Table 1). Obviously, both groups have different influences on the stabilisation of the ground as well as the first excited states in the corresponding compounds. Whereas the dimethylamino group seems to have a large stabilising effect on the electronic ground state as shown by their relatively large negative Hammett σ_X-value, the methylmercapto group seems to have a large stabilisation effect on the corresponding first excited state. As argument for the better ground state stabilisation of a Me_2N-group in comparison to a MeS-group in the studied tris(thienyl)methinium compounds the ^{13}C NMR shifts of the central C-atoms which correlate with the electron density and are found at 142.1 ppm for **7b** and at 149.1 ppm for **12** can be considered.[12]

The spectral effects of the methylmercapto group in the series of tris(2-thienyl)methinium ions observed here differ significantly from those in the series of some higher homologues of thiophene



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Scheme 3.

methine compounds reported by other authors.[13] Thus, for the tris[5(5′-methylmercapto)-2,2′-bithiophene]methinium perchlorate an absorption maximum at 370 nm has been reported. This value is more than 200 nm hypsochromically shifted in respect to the absorption maximum of compound **12**. Experiments to study this discrepancy are under way and their results will be reported in due course.

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References and Notes

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8 ^1H NMR data for compounds **7b** and **10–13** (measured in DMSO-D6): **7b**: 3.19 (s, 18H, NCH_3), 6.57 (d, $J = 4.8$ Hz, 3H, CH), 7.63 (d, $J = 4.8$ Hz, 3H, CH); **10**: 2.68 (s, 6H, SCH_3), 3.58 (s, 6H, NCH_3), 7.28 (d, $J = 4.2$ Hz, 3H, CH), 7.48 (d, $J = 6.0$ Hz, 2H, CH), 8.08 (d, $J = 6.0$ Hz, 1H, CH); **11**: 2.65 (s, 3H, SCH_3), 3.32 (s, 12H, NCH_3), 6.76 (d, $J = 5.1$ Hz, 2H, CH), 7.25 (d, $J = 3.6$ Hz, 1H, CH), 7.41 (d, $J = 3.9$ Hz, 1H, CH), 7.67 (d, $J = 4.8$ Hz, 2H, CH); **12**: 2.47 (s, 9H, SCH_3), 6.80 (d, $J = 4.2$ Hz, 3H, CH), 6.95 (d, $J = 4.2$ Hz, 3H, CH); **13**: 2.47 (s, 6H, SCH_3), 6.80 (d, $J = 3.9$ Hz, 2H, CH), 6.95–6.98 (m, 4H, CH), 7.45 (dd, $J = 4.8$ Hz, 1H, CH).
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Table 1. Spectral data of some tris(2-thienyl)methinium perchlorates and some of their carbocyclic analogues, measured in a) CF_3COOH or b) dichloromethane

Nr	X	Y	Z	λ_{max}/nm (log ε)	Ref.
7a	—	—	—	472 (4.55), 367 (3.69)[a]	[10]
7b	—	—	—	607 (4.89), 334 (4.26)[b]	
10	—	—	—	562 (4.40), 555 (4.40)[b]	
11	—	—	—	617 (4.75), 500 (3.89)[b]	
12	—	—	—	614 (4.89), 336 (4.12)[b]	
13	—	—	—	620 (4.86), 490 (4.44), 324 (3.85)[b]	
14a	H	H	H	431 (5.17)	[10]
14b	NMe_2	H	H	490	[10]
14c	NMe_2	NMe_2	H	620	[10]
14d	NMe_2	NMe_2	NMe_2	585	[10]
14e	SMe	H	H	547	[10],[11]
14f	SMe	SMe	H	595	[10],[11]
14g	SMe	SMe	SMe	586	[10],[11]