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Preparation and Characterization of 2-Amino-5-thienyl-Substituted Multicharged Methinium Compounds

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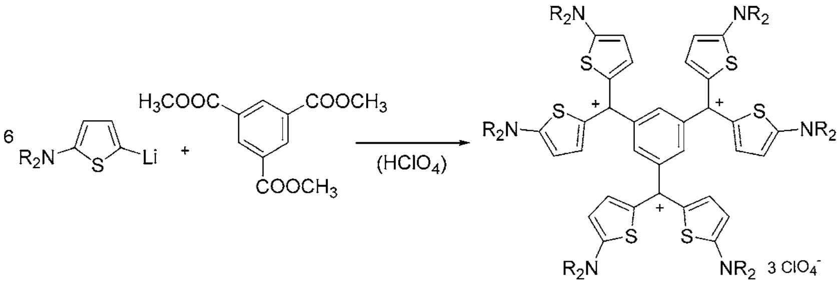
ABSTRACT



A series of new 2-amino-5-thienyl-substituted multicharged methinium compounds have been prepared and characterized spectroscopically and electrochemically by reaction of lithiated species of *N*,*N*-disubstituted 2-aminothiophenes with alkyl derivatives of di- and tricarbonic acids and subseqeunt addition of perchloric acid.

In the last three decades, *N*,*N*-disubstituted 2-amino-thiophenes **2** received a lot of interest. As heterocyclic analogues of the well-known *N*,*N*-disubstituted anilines **1**, which are important starting compounds for the synthesis of organic dyes,[1] they have been used as versatile educts for preparing different types of organic dyes as well. Thus, *N*,*N*-disubstituted 2-amino-thiophenes **2**[2] could be successfully transformed, especially if they are 5*H*-substituted, e.g., into azo dyes,[3] methine and azomethine dyes,[2b,4] or squarylium[5] and croconium dyes.[6] Very recently, they have been used as starting materials for a series of heterocyclic Crystal Violet analogues.[7]

The use of *N*,*N*-disubstituted 2-amino-thiophenes **2** as dye educts results in both deeply colored compounds and a high reactivity toward the corresponding dye-forming reagents,

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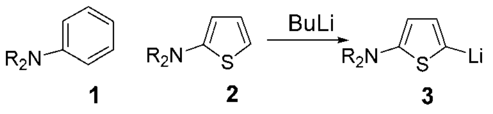
which usually react with the 2-amino-thiophenes **2** under very mild conditions.

Scheme 1

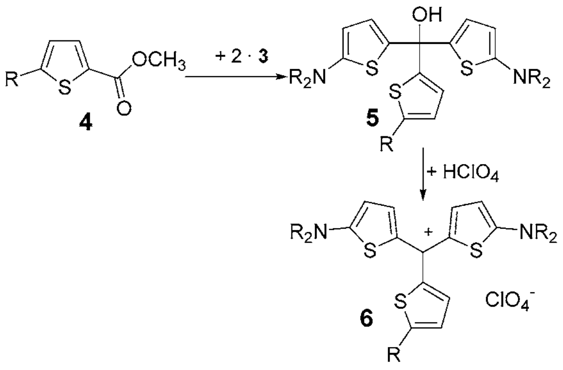


1 2 3

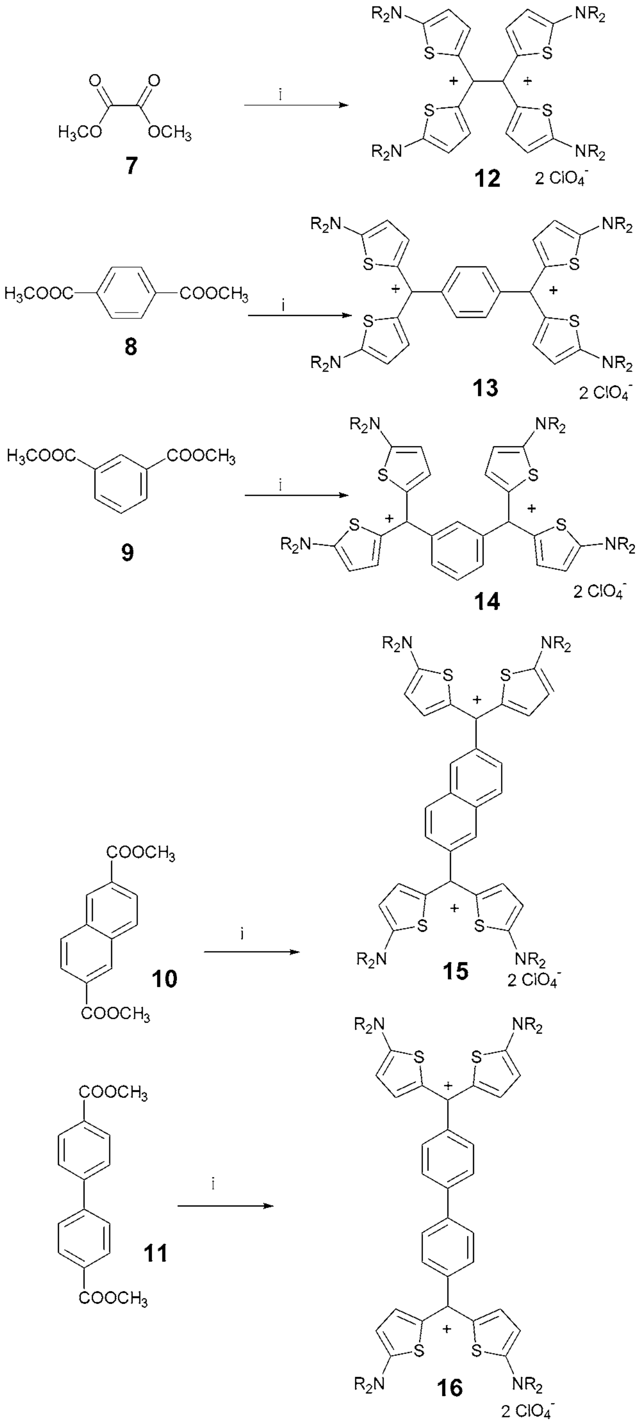
2, 3	R_2N
a	Me_2N
b	morpholino
c	Ph_2N

As far as less reactive electrophiles were allowed to react with *N*,*N*-disubstituted 2-amino-thiophenes **2**, the desired dye-forming reaction can fail to occur. In such cases, however, the reactivity of the *N*,*N*-disubstituted 2-amino-thiophenes **2** can be raised by transforming them into lithiated species **3**. This transformation can be caused, as reported recently,[8,9] very simply by reaction with lithium butyl in an indifferent solvent, such as *n*-hexane. The lithiated 2-amino-thiophene derivatives **3** so obtained are able to react with lesser reactive electrophiles. Thus, with trialkyl chlorostannanes they yield 5-stannylated 2-aminothiophenes which are versatile educts, e.g., for the synthesis of special 5-aryl-substituted 2-aminothiophenes.[9] Analogously, they can react with alkyl thiophene-2-carboxylates **4** to yield *N*,*N*-dialkyl-amino-substituted tris-(2-thienyl)methanols **5**, which by their reaction with mineralic acid, such as with perchloric acid, yield deeply colored methinium compounds **6**.[10]

Scheme 2



Scheme 3[a]



[a] Reagents: (i) (a) 4·**3**. (b) 2·$HClO_4$.

Now we report on the use of the lithiated 2-amino-thiophenes **3** as versatile reagents for the synthesis of a series of multicharged methinium compounds. Such compounds are hitherto unknown, in contrast to some multicharged methinium compounds derived from other lithiated thiophenes, such as 2-methylmercapto-5-lithiothiophene,.[11]

Multicharged methinium compounds derived from *N*,*N*-disubstituted 2-amino-thiophenes **2** can be easily prepared by reaction of the lithiated 2-amino-thiophens **3** with the alkyl derivatives of several di- and tricarbonic acids, such as with compounds **7**−**11**, in the required stoichiometric ratio. Thus,

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Table 1. Yield, Absorption Data, and Redox Potentials Including Radicals of Multicharged Methinium Perchlorates **12**−**16**, **19**, and **20**

compd	yield [%]	λ_{max}[nm] (log ε)[a]	E_{RED} [V][b]	n[c]	E_{OX} [V][b]	n[c]	ESR[e,f] [V]
12b	25	619 (4.94)	−1.14 (qrev) to −1.11 (qrev)d	2	+0.50 (rev), +0.46 (rev)[d]	2	+0.8
13b	53	610 (4.95)	−1.05 (qrev) to − 0.90 (rev)[d]	2	+0.46 (rev), +0.46 (rev)[d]	2	
14b	27	600 (5.20)	−0.95 (qrev) to − 1.05(rev)[d]	2	+0.47 (qrev), +0.46 (rev)[d]	2	
15b	61	617 (4.12)	−0.96 (qrev) to − 0.98 (rev)[d]	2	+0.46 (rev), +0.47 (rev)[d]	2	
16a	52	607 (4.97)	−1.20 (qrev)	2	+0.41 (rev)	2	
16b	23	610 (4.72)	−0.89 (qrev) to − 1.06 (rev)[d]	2	+0.47 (rev), +0.47 (rev)[d]	2	
16c	88	650 (5.08)	−0.79 (rev)	2	+0.62 (rev)	2	
19b	31	610 (4.85)	−0.83 (qrev) to − 0.95(qrev)[d]	3	+0.47 (qrev), +0.46(qrev)[d]	3	
19c	25	640 (5.08)	−0.78 (qrev)	3	+0.68(qrev)	3	−0.8 V/+0.8 V
20a	13	600 (4.93)	−1.19 (qrev)	1	+0.41(qrev)	1	
20b	65	615 (4.99)	−1.05 (qrev) to − 1.07 (rev)[d]	1	+0.46 (rev), +0.47 (rev)[d]	1	−1.2/+0.7
20c	78	680 (5.08)	−0.78 (qrev)	1	+0.63 (qrev)	1	

[a] Measured in dichloromethane. [b] Measured in acetonitrile with an glass-carbon electrode, containing tetrabutylammonium tetrafluoroborate, versus ferrocene/ferrocenium as internal standard, 100 mV/s scan rate; rev = reversible, qrev = quasireversible. [c] Number of electrons transferred. [d] Measured in benzonitrile with an platinium electrode, containing tetrabutylammonium tetrafluoroborate, versus ferrocene/ferrocenium as internal standard, 100 mV/s scan rate. [e] Measured in acetonitrile with a platinium mesh electrode, contaning tetrabutylammonium tetrafluoroborate, versus ferrocene/ferrocenium as external standard, 10 mV/s scan rate. [f] Potential at which a maximum ESR signal could be detected (from spectroelectrochemical data[12]).

by reaction of dimethyl oxalate **7**, dimethyl terephthalate **8**, dimethyl isophthalate **9**, dimethyl naphthalene-2,6-dicarboxylate **10**, or dimethyl biphenyl-4,4′-dicarboxylate **11** with, at least, 4 equiv of a *N*,*N*-disubstituted 2-amino-5-lithiothiophene **3** the corresponding bis-carbinolates were formed. The appropriated bis-cations **12**−**16** respectively were obtained by addition of perchloric acid to the reaction mixture. The 2-(dimethylamino)-, 2-morpholino-, and 2-diphenylamino-substituted derivatives **3a**−**c** have been used hitherto as lithiated 2-aminothiophenes.

Starting with trimethyl trimesicate **17** and using at least 6 equiv of a lithiated 2-aminothiophene **3** the hexa-(2-amino-5-thienyl)-substituted tris-cations **19** were obtained analogously. Furthermore, methyl benzoate **18** yields the monocationic species **20** as well. These compounds can be considered as the parent compounds of the multicharged methines **12**−**16** and **19**. They are structurally related to the well-known Malachite Green dyes and exhibit a deep color and a considerable stability, too.[10]

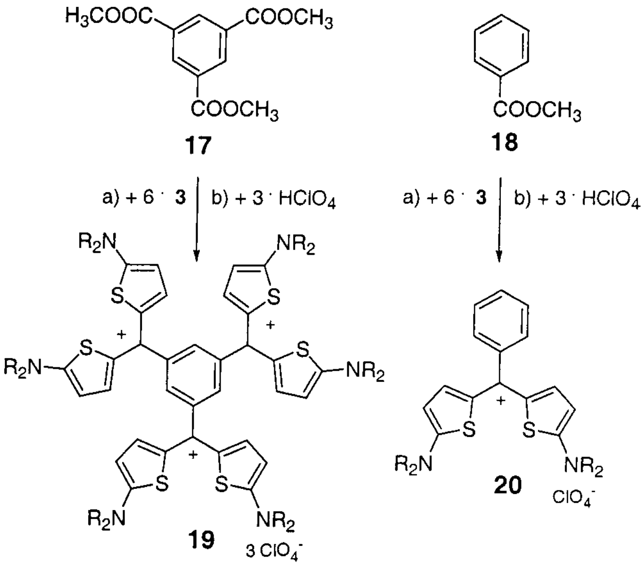
Most of the multicharged methinium compounds could be obtained (see Table 1) in moderate yields with the route described above. Although in many cases intermediate carbinols (or their lithium salts) were obtained as well-defined compounds, these precursors were not isolated in analytic grade but were transformed, as mentioned before, into their corresponding cationic species by reaction with perchloric acid.

The structures of all cationic compounds **12**−**16**, **19**, and **20** prepared were confirmed by elemental analysis and NMR spectroscopy. Some of these data are available as Supporting Information. All cationic compounds prepared were studied by means of UV/vis spectroscopy and cyclic voltammetry.

As can be seen from Table 1, in which the spectral data of the compounds prepared are depicted, all cationic compounds exhibit intense absorptions in the visible spectral range: their positions were found between 610 and 670 nm depending on the substitution pattern at their *N*-atoms, as well as on the number and relative arrangement of their (2-amino-5-thienyl)-substituted methine moieties at the appropriate core derived from the alkyl carboxylates used for their synthesis.

The electrochemical data for all positive charged methinium compounds demonstrate both cathodic and, what is more remarkably, anodic reactions. The reduction potentials were found in the range of −0.78 to −1.2 V whereas the oxidation potentials were detected in the range from +0.40 to +0.63 V.

Scheme 4



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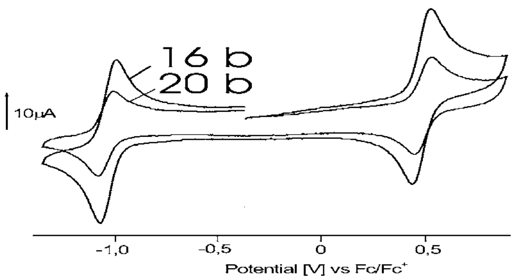

Figure 1. Cyclic voltammograms of compound **16b** (2 × 10^{-4} M) and **20b** (2 × 10^{-4} M) measured in benzonitrile, contaning 0.1 M tetrabutylammonium tetrafluoroborate, scan rate 100 mV/s.

As all of the multicharged compounds studied are less soluble in most of the usual organic solvent that have been studied by cyclic voltammetry in strong polar solvents, sucg as acetonitrile or benzonitrile. As an example, the voltammetric behavior of compounds **16b** and **20b** is given in Figure 1.

Compounds **16b** and **20b** are, like the other cationic compounds studied, both reducible and oxidizable reversibly. The charge transfer in solution is shown to be a one-electron process per chromophore unit in the anodic and cathodic range. During reduction, the electrode can be rapidly covered by a reaction layer, which hinders further electron transfer. Thus, the corresponding electron transfer can turn out to be irreversible.

The elctrochemical potentials given in Table 1 depend, at first glance, more on the amino substituents than on the number and position of the methinium moieties. Thus, the *N*,*N*-diphenyl-substituted species **16c** and **20c** exhibit lower reduction potentials as their *N*,*N*-dialkylated congeners **16a**, **16b**, **20a**, and **20b**, respectively. In a similar way the oxidation potentials of *N*,*N*-diphenyl-substituted compounds **16c** and **20c** are shifted to more positive potentials than those of their *N*,*N*-dialkyl-substituted derivatives.

Due to their high tendency to form reduced as well as oxidized species under relatively mild conditions mono- and multicharged methinium compounds under study are hopeful candidates for stabilized open-shell systems. Persistent radicals have been detected in several cases by ESR spectroscopy. The analysis of these spectra is, due to a strong coupling of the electron spins with protons, rather complicated and will be reported in detail after further studies.

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Supporting Information Available: Experimental procedure for preparing **12**−**16**, **19**, and **20** and their ^{1}H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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