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Synthesis and spectral characterisation of a series of new heterocyclic triphenylmethane analogues

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Dedicated to the memory of Professor Masaru Matsuoka.

Abstract

By condensation of *N,N′*-persubstituted bis-(2-aminophenyl)ketones **4**, bis-(2-amino-5-thienyl)ketones **16**, 2-amino-5-thienyl-(2-amino-5-thiazolyl)ketones **17**, and bis-(2-amino-5-thiazolyl)ketones **18** as well as of *N*-disubstituted derivaties of alkyl 2-aminothiophene-5-carboxylates **12**, alkyl 2-aminothiazole-5-carboxylates **15** and 2-amino-5-thienyl(2-thienyl) ketones **29** with *N*-disubstituted anilines **1**, 2-aminothiophenes **2**, 2-aminothiazoles **3**, and 2-methylmercaptothiophenes **34** or their lithiated derivatives a series hitherto unknown heterocyclic Crystal Violet analogues **6–8**, **19–25**, and **40–48** have been prepared and characterised spectroscopically.

Keywords: Bis(hetaryl)ketones; Tris-(2-amino-5-thienyl)methinium salts; tris-(2-methylmercapto-5-thienyl)methinium salts; UV–vis absorption spectra

1. Introduction

In the past three decades *N,N*-disubstituted 2-amino-thiophenes **2** and 2-aminothiazoles **3** have received much interest. As heteroanalogues 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. Thus, *N,N*-disubstituted 2-amino-thiophenes **2** [2] can be successfully transformed, especially if they are unsubstituted at their 5-position, for example, into azo dyes [3], methine and azomethine dyes [2b,4], or squarylium [5] and croconium dyes [6]. Analogously, *N,N*-disubstitued 2-aminothiazoles **3** [7] have been transformed into corresponding azo dyes [8], methine and azamethine dyes [9], as well as into squarylium [10] and tricyanovinyl dyes [11]. Several of the dyes derived from the heterocyclic amines **2** and **3** are of technical interest. For instance, a variety of 2-aminothiophene methine dyes exhibit highly non-linear optical (NLO) properties [12] or enhanced photorefractive [13] properties so that they have been claimed for manufacturing of materials with NLO or photorefractive applications. Special 5-acceptor-substituted 2-amino-thiophenes exhibit an extremely large positive solvatochromism which enables the use of these

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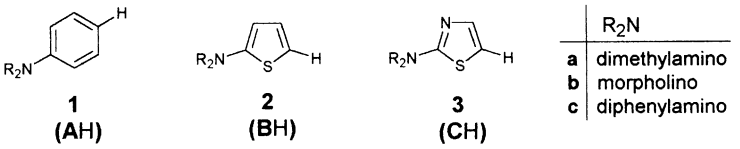
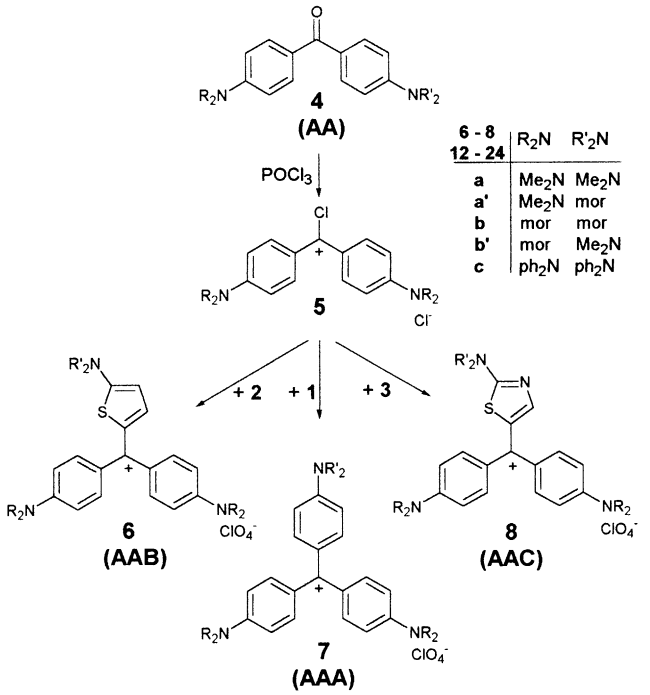


Scheme 1.

compounds as indicators for measuring the polarity of solvent [14]. On the other hand, azo dyes derived from 4-(2,4-diamio-5-thiazolyl)substituted 2-aminothiazoles exhibit extremely long-wavelength absorption maxima, whose positions are also strongly influenced by solvent polarity [15]. In contrast to the afore-mentioned 5-acceptor-substituted 2-aminothiophenes, they exhibit negative solvatochromism (Scheme 1).

2. Results and discussion

Despite their manifold use as starting materials for new chromophores with interesting properties, *N*-disubstituted 2-amino-thiophenes **2** and 2-amino-thiazoles **3** have not been used for the synthesis of heterocyclic analogues of the well-know Crystal Violet dyes. However, this can be done, as we found very recently [16], if Michler's Ketone **4** was treated analogously to the reported synthesis of Crystal Violet **7a** from dimethylaniline **1a** and Michler's Ketone **4a** [17], with one of the heterocyclic compound **2** or **3** in presence of $POCl_3$ as acidic condensation reagent. The reaction proceeds via the intermediate bis[4-(dimethylamino)-phenyl] chloromethinium chlorides **5,** which, due to their strong electrophilic character, react with the electron-rich (het)arylamine used as co-reagent. The products formed were advantageously isolated as perchlorates by addition of perchloric acid to the resultant reaction mixture (Scheme 2).



Scheme 2.

To extend the synthesis of the heterocyclic Crystal Violet derivatives of structure **6** and **8,** heterocyclic analogues of Michler's Ketones were required. Until recently, such compounds were unknown, but we found that they could be synthesised by a simple procedure starting from *N,N*-persubstituted thioacrylamides **9** [18] or their aza derivatives **11** [19]. These starting materials can be prepared from easily available educts, such as by reaction of *N,N*-persubstituted 1-chlorovinamidinium salts [20] with sodium sulphide [21] or by reaction of *N,N*-disubstituted thioureas [22] with dimethylformamide acetals [23]. They can then be transformed, as depicted in Scheme 3, into heterocyclic ketones, such as compounds **16**, **17**, and **18**, by their reaction with 1,3-dichloropropan-2-one **10a**. The reaction was advantageously performed by heating the required components in an indifferent solvent, such acetonitrile, in presence of a base (e.g. triethylamine), and could be directed in such a way that either the bis-ketones **16** and **18** or the mono-ketones **13** and **14** were obtained [24]. The last-mentioned compounds could be used as educts for the synthesis of the unsymmetrical bis-ketones **17** also, if they were allowed to react with a second equivalent of a *N,N*-persubstituted thioacrylamide **9** or its aza derivative **11**. Hence, all necessary starting materials for the synthesis of a closed series of thiophene and thiazole analogues of Crystal Violet were available.

The *N,N*-persubstituted thioacrylamides **9** and their aza derivatives **11** have been used also for the synthesis of methyl 2-aminothiophene-5-carboxylates **12** [25] and 2-aminothiazole-5-carboxylates **15** [26], which provide versatile starting materials for the synthesis of a series of heterocyclic Crystal Violet derivatives, by their reaction with methyl bromoacetate **10b** under the same conditions as used for the synthesis of the aforementioned mono- and bis-ketones **13**, **14**, and **16–18**.

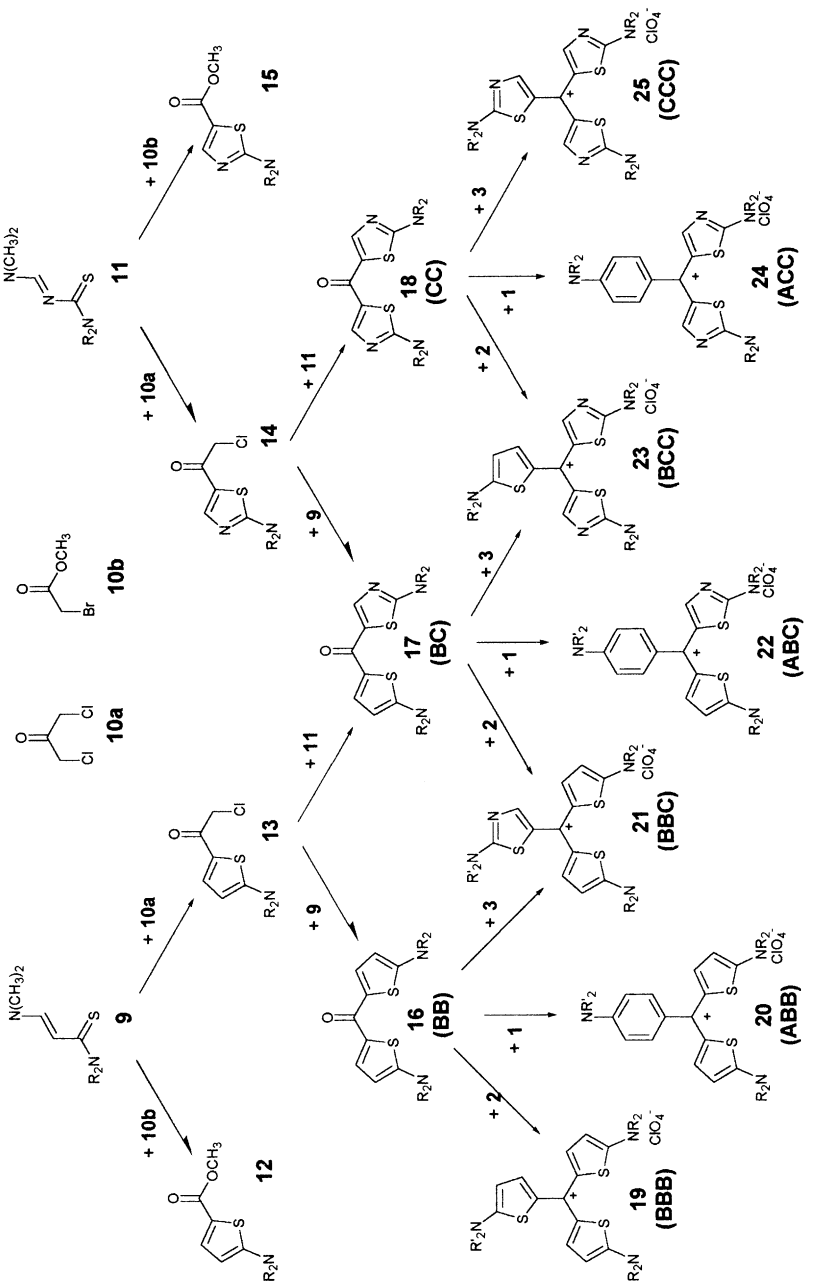
The preparation of heterocyclic Crystal Violet derivatives from the bis-hetaryl ketones **16–18** has been performed in the same way as described above, namely by allowing these ketones to react with one of the carbocyclic or heterocyclic amines **1–3** in the presence of $POCl_3$. The reactions involve the intermediate bis(hetaryl)chlormethiniminium salts **26** and, depending on the educts used, give rise to the heterocyclic Crystal Violet derivatives **19–25**, which were also isolated as perchlorate salts.

Because in some cases only low yields of products were obtained, presumably due to the high stability of the first formed bis(hetaryl)chlormethiniminium salts **26**, a second method for preparing the same heterocyclic Crystal Violet derivatives was developed, namely Method B, Scheme 4. This method involved reacting the same bis-ketones **16–18** with the lithiated derivative (**ALi**, **BLi**, or **CLi**) of the amines **1–3**. The reaction involves formation of the corresponding lithium carbinolates **27**, from which the desired Crystal Violet derivates **19–25** were obtained by addition of perchloric acid to the reaction mixture.

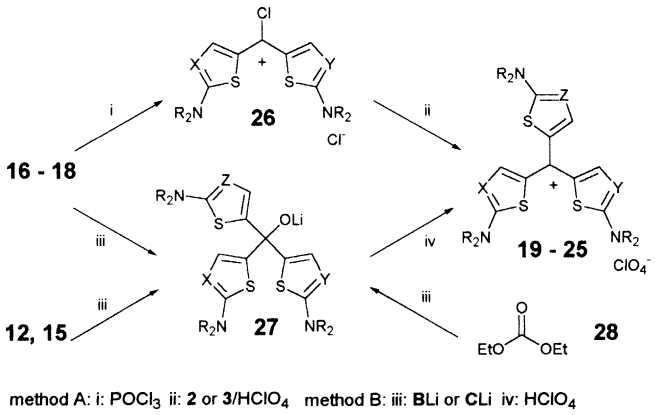
The advantage of method B is that it can also be used for the synthesis of heterocyclic Crystal Violet analogues by using the methyl carboxylates **12** and **15** as starting materials, or in special cases, using diethyl carbonate **28**. However, the carboxylate esters require reaction with two or three equivalents of the lithiated derivatives of the carbocyclic or heterocyclic amines **1–3**. The reactions involve the intermediacy of the te lithium tris(het) aryl-substituted carbinolates **27,** which can then be converted into the corresponding methinium perchlorates by reaction with perchloric acid.

In Table 1 all the new Crystal Violet derivatives prepared and the methods used for their synthesis are listed. As can be seen, by using the mentioned methods, the complete series of heterocyclic analogues of Crystal Violet is available. Although in the most cases morpholino-substituted derivatives have been prepared, these methods are also useful for the preparation of other *N*-substituted derivatives, such as the synthesis of *N*-(diphenylamino)-substituted compounds which possess further π-electron moieties at their *N*-atoms.

The synthetic concept used for the synthesis of the reported series of heterocyclic Crystal Violet analogues can also be applied to the synthesis of several hitherto unknown differently substituted tris(2-thienyl)methinium salts, particularly those with methylmercapto substituents in the thienyl rings. The methylmercapto group was found more than seventy years ago [27] to act as a strong auxochrome in compounds of the triphenylmethinium



Scheme 3.



Scheme 4.

series, and can shift the absorption maximum of the unsubstituted parent compound bathochromically to a similar extent as a dialkylamino group. Thus it was of interest to examine the effects of this group as an auxochrome in the tris(2-thienyl)methinium dye series.

As starting materials for the synthesis of a series of different methylmercapto-substituted tris(2-thienyl) methinium salts, the bis-(2-amino-5-thienyl) ketones **16** as well as the methyl 2-dialkylamino-thienyl-5-carboxylates **12**, and diethyl carbonate **28** have been used. Additionally, the 5-dimethylamino-substituted bis(2-thienyl)ketone **29** and methyl 2-methylmercaptothienyl-5-carboxylate **37** were used. The ketone **29** was prepared analogously to the bis(2-amino-5-thienyl)ketones **16,** by reaction of *N,N′*-tetramethyl-3-aminothioacrylamide **9a** with 2-bromoacetylthiophene, whereas the ester **37** was prepared from 2-methylmercaptothiophene **34** via its lithio derivatives **35** and **36** by subsequent reaction of these compounds with lithium butyl, carbon dioxide, and methyl iodide, respectively (Scheme 5).

For preparing the required methylmercapto-substituted tris(2-thienyl)methinium salts these starting materials were allowed to react, according to method B, with several lithiated compounds, such as 2-lithiothiophene **31**, 2-mercapto-5-lithiothiophene **35**, 2-dimethylamino-5-lithiothiophene **38,** which in turn were prepared from their corresponding H-substituted parent compounds by their reaction with lithium butyl, followed by addition of perchloric acid to the reaction mixture.

The compounds so prepared are depicted in Scheme 6.

All the heterocyclic Crystal Violet analogues described here are, as expected, deeply coloured compounds. Their structures were confirmed by elemental analysis and NMR spectroscopy (see Table 2). Thus, in the ^{1}H NMR spectra characteristic signals at about 6.90 and 8.00 ppm were present. These signals can be attributed to the protons in the aromatic or heteroaromatic moieties, and exhibit characteristic coupling constants for adjacent protons. In the ^{13}C NMR spectra, signals for the aromatic or heteroaromatic C-atoms as well as for the central methine atom were detected between 120 and 200 ppm. At first glance it is difficult to attribute all the ^{13}C NMR signals unambiguously to their appropriate C-atoms. Therefore a theoretical approach was used to facilitate correct assignments [28]. Accordingly, it was noted that the chemical shift of the central methine atoms depended significantly on the nature of the attached carbocyclic or heterocyclic moieties. For instance, the δ-value of the central methine carbon atom in Crystal Violet **7a** occurred at 170.6 ppm whereas the δ-value for the same C-atom in tris(2-dimethylamino-5-thienyl)methinium perchlorate **19a** was at 142.1 ppm. Both signals are shifted by nearly 30 ppm towards lower fields relative to their unsubstituted parent compounds, as indicated by the ^{13}C NMR data of

Table 1
Characterisation data for bis-(aryl)-hetaryl-, aryl-bis-(hetaryl)- and tris-(hetaryl)-methinium perchlorates

No. (code)[a]	R^1	R^2	R^3	Yield (%)	Precursors	mp (°C)	Formula calcd. found	C	H	N	S
6a	$N(CH_2)_2O$	$N(CH_3)_2$	$N(CH_3)_2$	38.7 (B)	**1a/12b**	156–161	$C_{25}H_{30}ClN_3O_5S$	57.74	5.82	8.08	6.17
(**aaB**)							(520.01)	57.51	5.79	7.92	5.98
6b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	41.2 (B)	**1b/12b**	161–163	$C_{29}H_{34}ClN_3O_7S$	57.66	5.67	6.96	5.31
(**AAB**)							(604.08)	57.47	5.89	6.43	4.93
7b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	23.4 (B)	**1b/28**	>360	$C_{31}H_{36}ClN_3O_7$	62.25	6.07	7.03	–
(**AAA**)							(598.07)	62.49	6.28	6.88	
8a	$N(CH_2)_2O$	$N(CH_3)_2$	$N(CH_3)_2$	23.8 (B)	**1a/15b**	158–163	$C_{24}H_{29}ClN_4O_5S$	55.32	5.61	10.75	6.15
(**aaC**)							(521.00)	55.14	5.18	10.59	5.97
8b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	25.0 (B)	**1b/15b**	225–228	$C_{28}H_{33}ClN_4O_7S$	55.58	5.50	9.26	5.30
(**AAC**)							(605.07)	55.44	4.91	9.03	5.18
19a′	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	12.6 (B)	**2a/12a**	>360	$C_{19}H_{24}ClN_3O_4S_3$	46.57	4.97	8.58	19.63
(**NNN**)							(490.03)	46.84	5.19	8.35	19.46
19a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	45.4 (B)	**2b/12a**	175–177	$C_{23}H_{28}ClN_3O_6S_3$	48.12	4.92	7.32	16.75
(**bBB**)							(574.09)	47.89	4.54	6.94	17.03
19b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	39.9 (A)	**2b/16b**	>360	$C_{25}H_{30}ClN_3O_7S_3$	48.73	4.91	6.82	15.61
(**BBB**)				21.2 (B)	**2b/12b**		(616.13)	48.52	5.14	6.68	15.17
				20.5 (B)	**2b/28**						
20a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	90.7 (A)	**1a/16a**	224–225	$C_{25}H_{30}ClN_3O_6S_2$	52.85	5.32	7.40	11.29
(**aBB**)				8.5 (B)	**1a/16a**		(568.07)	52.71	5.25	7.56	10.86
20b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	7.9 (A)	**1b/16b**	206–209	$C_{27}H_{32}ClN_3O_7S_2$	53.15	5.29	6.89	10.51
(**ABB**)				16.5 (B)	**1b/16b**		(610.11)	52.93	4.97	6.56	10.04
21a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	16.0 (B)	**2b/15a**	>360	$C_{22}H_{27}ClN_4O_6S_3$	45.94	4.73	9.74	16.72
(**BBc**)							(575.08)	46.21	4.94	9.91	16.67
21b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	7.8 (A)	**3b/16b**	235–242	$C_{24}H_{29}ClN_4O_7S_3$	46.71	4.74	9.08	15.59
(**BBC**)				22.2 (B)	**2b/15b**		(617.12)	46.54	4.43	8.87	15.32
				7.4 (B)	**3b/16b**						
22a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	17.1 (B)	**1a/17b**	165–168	$C_{24}H_{29}ClN_4O_6S_2$	50.65	5.14	9.85	11.27
(**aBC**)							(569.06)	50.96	4.98	9.35	10.89
22b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	5.8 (B)	**1b/17b**	163–165	$C_{26}H_{31}ClN_4O_7S_2$	51.10	5.11	9.17	10.49
(**ABC**)							(611.09)	51.56	5.65	9.34	10.87
23a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	8.4 (B)	**3b/12a**	169–170	$C_{21}H_{26}ClN_5O_6S_3$	43.78	4.55	12.16	16.70
(**bCC**)							(576.07)	44.15	4.43	11.89	16.91
23b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	Traces (A)	**2b/18b**	275–280	$C_{23}H_{28}ClN_5O_7S_3$	44.69	4.57	11.33	15.56
(**BCC**)				25.4 (B)	**3b/12b**		(618.11)	44.12	4.43	10.89	15.20
24a	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_3)_2$	Traces (A)	**1a/18b**	164–167	$C_{23}H_{28}ClN_5O_6S_2$	48.46	4.95	12.29	11.25
(**aCC**)				3.2 (B)			(570.05)	48.47	4.35	12.44	11.04
24b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	Traces (A)	**1b/18b**	114–115	$C_{25}H_{30}ClN_5O_7S_2$	49.05	4.94	11.44	10.48
(**ACC**)				26.3 (B)	**1b/18b**		(612.08)	49.38	5.03	11.34	10.90
25b	$N(CH_2)_2O$	$N(CH_2)_2O$	$N(CH_2)_2O$	Traces (A)	**3b/18b**	171–173	$C_{22}H_{27}ClN_6O_7S_3$	42.68	4.40	13.57	15.54
(**CCC**)				20.1 (B)	**3b/15b**		(619.19)	42.43	4.05	12.98	15.13
40	$N(CH_3)_2$	SCH_3	SCH_3	19.0 (B)	**34/12a**	75–80	$C_{17}H_{18}ClNO_4S_5$	41.16	3.66	2.82	32.31
(**NSS**)							(496.06)	41.25	4.02	2.91	31.91
41	SCH_3	SCH_3	SCH_3	22.0 (B)	**34/28**	168–170	$C_{16}H_{15}ClO_4S_6$	38.50	3.03	–	38.54
(**SSS**)							(499.08)	38.59	3.45		38.23
42	SCH_3	SCH_3	H	15.6 (B)	**34/33**	184–185	$C_{15}H_{13}ClO_4S_5$	39.77	2.89	–	35.39
(**HSS**)							(453.00)	39.60	3.17		35.29
43	$N(CH_3)_2$	H	H	27.5 (B)	**30/12a**	93–95	$C_{15}H_{14}ClNO_4S_3$	44.60	3.49	3.47	23.81
(**HHN**)							(403.89)	45.07	4.02	3.41	21.12

(*continued on next page*)

Table 1 (*continued*)

No. (code)[a]	R^1	R^2	R^3	Yield (%)	Precursors	mp (°C)	Formula calcd. found	C	H	N	S
44 (HHH)	H	H	H	50.0 (B)	**30/28**	>320	$C_{13}H_9ClO_4S_3$ (360.82)	43.27 43.21	2.51 2.86	–	26.66 26.57
45 (HNN)	$N(CH_3)_2$	$N(CH_3)_2$	H	44.7 (B)	**2a/33**	233–235	$C_{17}H_{19}ClN_2O_4S_3$ (446.96)	45.68 45.12	4.28 4.48	6.27 6.27	21.52 21.78
46 (NNS)	$N(CH_3)_2$	$N(CH_3)_2$	SCH_3	3.9 (B)	**34/16a**	180–183	$C_{18}H_{21}ClN_2O_4S_4$ (493.05)	43.85 43.68	4.29 4.45	5.68 5.81	26.01 26.24
47 (HHS)	SCH_3	H	H	67.9 (B)	**30/37**	75–76	$C_{14}H_{11}ClO_4S_4$ (406.91)	41.32 41.79	2.72 2.74	–	31.52 31.69
48 (HNS)	$N(CH_3)_2$	SCH_3	H	12.8 (B)	**34/29**	112–113	$C_{16}H_{16}ClNO_4S_4$ (450.01)	42.70	3.58	3.11	28.50

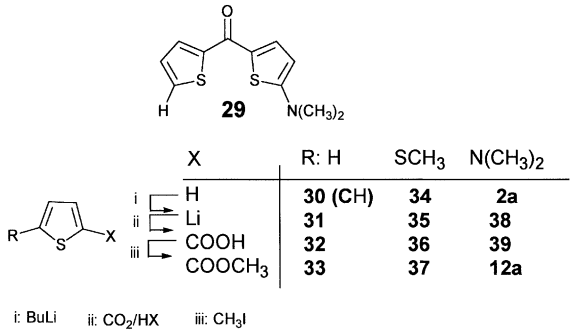
[a] Depiction of the type of attached aromatic rings, or substitution pattern, in the dye perchlorate; for the meanings of the letters, see Schemes 1–6.

triphenylmethinium perchlorate and tris(2-thienyl)methinium perchlorate.

It is worth mentioning that the ^{13}C chemical shifts of the central methine C-atom in tris(2-methylmercapto-5-thienyl)methinium perchlorate **40** is found with 149.1 ppm some higher than for the same C-atom in tris(2-dimethylamino-5-thienyl)methinium perchlorate **19a**. These data indicate that the postive charge at the central methine moiety in the 2(dialkylamino-5-thienyl)-substituted methinium ions is more effectively delocalised than in corresponding 2(methylmercapto-5-thienyl)-substituted methinium ions.

As mentioned previously, all the tris(hetaryl) subtituted methinium perchlorates are deeply coloured compounds, their colour arising from intense absorption bands in the visible spectral range. The position of the longest-wavelength absorption band depends on the type of (het)aryl groups linked to the central methine moiety, as well as the substitution pattern within these groups. At first glance the spectral properties of the tris(hetaryl)subtituted methinium perchlorates are very similar to those of structurally related compounds in the triphenylmethine series. Thus the tris(2-dialkylamino-5-thienyl)methinium salts **19** exhibit almost the same longest absorption maximum wavelength as the Crystal Violet derivatives **7**. Their absorption data are compared in Table 3. This similarity of λ_{max} values also occurs between the bis(dialkylamino)-substituted and mono(dialkylamino)-subtituted derivatives in the triphenylmethinium and trithienylmethinium series. Both groups of compound exhibit two absorption bands in the visible region, and the λ_{max} value of the longest wavelength band is shifted to longer or shorter wavelength, respectively, in comparison with the λ_{max} value of the longest wavelength band of their tris(dialkylamino)substituted analogues. Thus, a slight bathochromic shift for these bands is observed on going from the tris (dialkylamino)substituted compounds **7** and **19** to the bis(dialkylamino)substituted compounds **51** and **45,** whereas a significant hypsochromic shift is observed on going from these bis(dialkylamino) substituted compounds to their mono(dialkylamino) substituted derivatives **50** and **43.** In all cases the shorter-wavelength absorption bands in the mono(dialkylamino)-substituted compounds of the trityl and tris(2-thienyl)methinium series are shifted to shorter wavelengths than the longest-wavelength maxima of the corresponding bis-substituted compounds (see Tables 2 and 3).

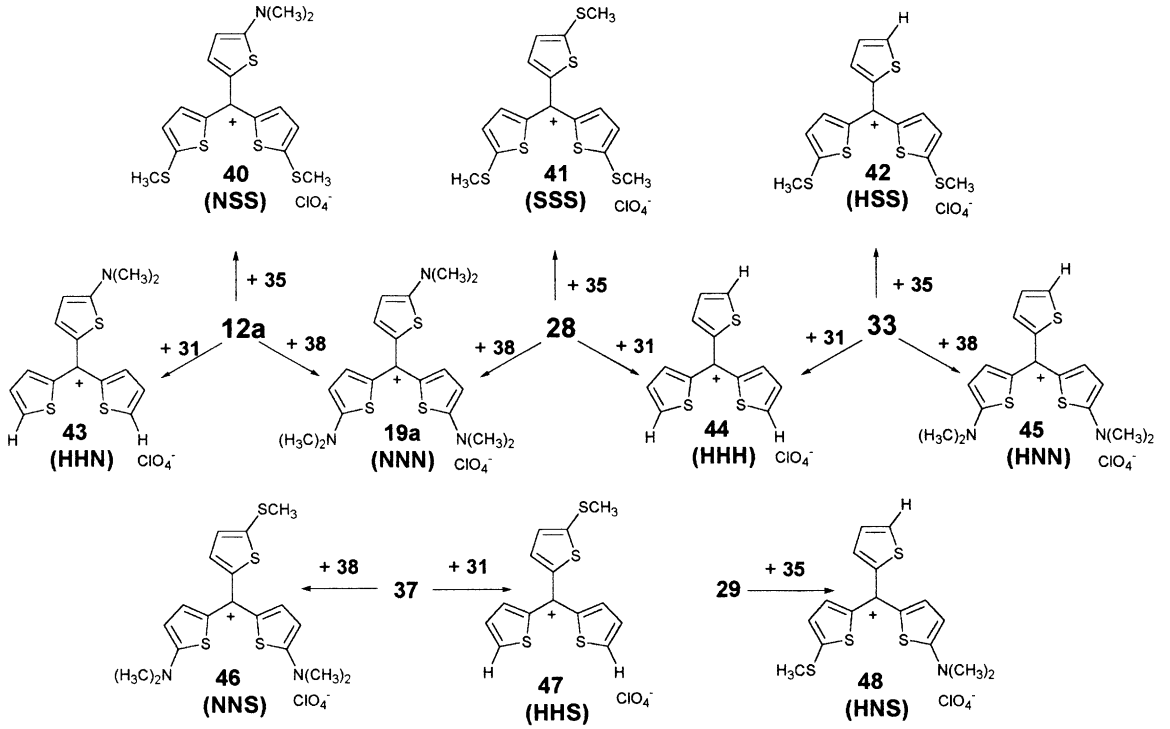
The same regularities can be observed with the methylmercapto-substiuted compounds of the trityl- and tris(2-thienyl)methinium series. On going from the tris(methylmercapto)-substituted compounds **41** and **52** to the bis-(methylmercapto)-substitiuted compounds **42** and **53** and the mono-(methylmercapto)substituted compounds **47** and **54**, at first a slight bathochromic, than a stronger hypsochromic effect of the longest-wavelength absorption band is observed. Remarkably, the longest-wavelength absorption maxima of the



Scheme 5.

methylmercapto-substituted compounds **41**, **42**, **47**, and **52–54** are found, in general, at almost the same wavelengths as those of the corresponding dialkylamino-substituted compounds **43**, **45**, **19a**, and **49–51**, respectively. In most cases, the absorption maxima of the mercapto-substituted compounds are slightly shifted to longer wavelengths in comparison to the dialkylamino-substituted compounds. Thus, the tris(2-methylmercapto-5-thienyl)methinium perchlorate **41** absorbs at slightly longer wavelengths than the tris-(4-dimethylaminophenyl)methinium perchlorate **19a**. These spectral relationships agree with those for the tris(methylmercapto)-substituted and tris(dialkylamino)-substituted derivatives **52** and **7a** in the trityl series, as documented in the earlier literature.

To gain more insight into the spectral relations found in the trityl and tris(thienyl)methinium series quantum chemical calculations in the framework of the PPP algorithm have been performed. Although this method is a semi-empirical one which is, owing to their restriction on the π-electrons, reasonably applicable only for molecules having a full planar structure of their conjugated π-system it has been used due to their satisfactory reproduction and simple interpretance of the UV/vis spectral data of compounds with an extended π-electron system. Accordingly to the results of a theoretical study for confirming the structure of the molecules studied as well as in respect to X-ray data of



Scheme 6.

Table 2
Spectroscopic data for the bis-(aryl)-hetaryl-, aryl-bis-(hetaryl)- and tris-(hetaryl)-methinium perchlorates

Comp (code)[a]	λ_{max} (log ε) [nm] in MC	^{1}H NMR, δ-values in ppm	^{13}C NMR δ-values in ppm	Solvent[b]
6a (**aaB**)	589 (4.94)	3.08 (*s*, 12H, CH_3), 3.80 (*m*, 8H, CH_2), 6.86 (*d*, 4H, CH), 7.18 (*d*, 2H, CH), 7.34 (*m*, 3H, CH), 7.81 (*d*, 1H, CH)	40.53, 51.49, 65.30, 111.83, 117.57, 125.26, 128.43, 135.16, 148.42, 153.30, 160.58, 178.45	[a]
6b (**AAB**)	582 (4.77)	3.37 (*t*, 8H, CH_2), 3.75 (*t*, 8H, CH_2), 3.83–3.86 (*m*, 8H, CH_2), 7.09 (*d*, 4H, CH), 7.20 (*d*, 2H, CH), 7.34 (*d*, 2H, CH), 7.48 (*d*, 1H, CH), 7.90 (*d*, 1H, CH)	46.72, 52.09, 65.17, 65.74, 113.43, 119.66, 127.50, 130.14, 134.23, 148.91, 153.23, 158.81, 179.66	[a]
7b (**AAA**)	597 (4.97)	3.63 (*t*, 12H, CH_2), 3.77 (*t*, 12H, CH_2), 7.21 (*d*, 6H, CH), 7.32 (*d*, 6H, CH)	46.56, 65.64, 113.42, 127.29, 139.25, 155.44, 176.53	[a]
8a (**aaC**)	579 (4.92)	3.19 (*s*, 12H, CH_3), 3.78 (*m*, 8H, CH_2), 6.96 (*d*, 4H, CH), 7.44 (*d*, 4H, CH), 8.01 (*s*, 1H, CH)	30.55, 49.26, 65.33, 112.75, 125.10, 128.10, 139.13, 155.28, 160.44, 164.92, 179.12	[a]
8b (**AAC**)	579 (4.92)	3.56 (*t*, 8H, CH_2), 3.76 (*t*, 8H, CH_2), 3.81 (*t*, 4H, CH_2), 3.85 (*t*, 4H, CH_2), 7.16 (*d*, 4H, CH), 7.45 (*d*, 4H, CH), 8.18 (*s*, 1H, CH)	46.49, 49.61, 65.11, 65.61, 113.46, 126.51, 129.22, 129.26, 136.79, 154.97, 162.86, 179.99	[a]
19a′ (**NNN**)	607 (4.89)	3.19 (*s*, 18H, $N(CH_3)_2$), 6.57 (*d*, 3H, CH), 7.63 (*d*, 3H, CH)	42.00, 108.88, 122.11, 141.81, 141.97, 170.59	[a]
19a (**bBB**)	612 (4.90)	3.26 (*s*, 6H, CH_3), 3.46 (*t*, 8H, CH_2), 3.76 (*t*, 8H, CH_2), 6.73–6.77 (*m*, 3H, CH), 7.64 (*d*, 2H, CH), 7.75 (*d*, 1H, CH)	42.43, 49.50, 64.97, 108.94, 111.48, 122.81, 123.38, 141.11, 142.23, 143.58, 169.70, 172.82	[a]
19b (**BBB**)	615 (4.97)	3.51 (*t*, 12H, CH_2), 3.77 (*t*, 12H, CH_2), 6.79 (*d*, 3H, CH), 7.68 (*d*, 3H, CH)	49.85, 65.15, 110.18, 123.23, 142.38, 142.89, 171.02	[a]
20a (**aBB**)	605 (5.03)	3.07 (*s*, 6H, CH_3), 3.62 (*t*, 8H, CH_2), 3.77 (*t*, 8H, CH_2), 6.85 (*d*, 2H, CH), 6.93 (*d*, 2H, CH), 7.34 (*d*, 2H, CH), 7.61 (*d*, 2H, CH)	40.96, 51.22, 66.60, 112.18, 112.29, 125.73, 126.98, 135.13, 146.31, 153.60, 153.85, 174.92	[a]
20b (**ABB**)	609 (4.83)	3.32 (*t*, 4H, CH_2), 3.63 (*t*, 8H, CH_2), 3.76 (*m*, 12H, CH_2), 6.90 (*d*, 2H, CH), 7.07 (*d*, 2H, CH), 7.33 (*d*, 2H, CH), 7.55 (*d*, 2H, CH)	46.99, 50.52, 65.26, 65.96, 112.54, 113.50, 125.13, 127.02, 133.17, 145.03, 150.35, 152.82, 173.56	[a]
21a (**BBc**)	618 (4.79)	3.02 (*s*, 6H, CH_3), 3.60 (*t*, 8H, CH_2), 3.78 (*t*, 8H, CH_2), 6.90 (*d*, 2H, CH), 7.76 (*s*, 1H, CH), 7.82 (*d*, 2H, CH) 7.74 (*s*, 1H, CH), 7.83 (*d*, 2H, CH)	39.50, 50.08, 64.93, 111.80, 122.11, 123.71, 140.23, 143.56, 151.07, 172.29, 174.62 139.99, 144.25, 150.36, 172.90, 174.82	[a]
21b (**BBC**)	623 (4.77)	3.62 (*t*, 12H, CH_2), 3.76 (*t*, 12H, CH_2), 6.92 (*d*, 2H, CH), 7.74 (*s*, 1H, CH), 7.83 (*d*, 2H, CH)	48.26, 50.45, 65.27, 112.48, 122.52, 124.18, 139.99, 144.25, 150.36, 172.90, 174.82	[a]
22a (**aBC**)	597 (4.73)	3.08 (*s*, 6H, CH_3), 3.63 (*m*, 8H, CH_2), 3.77 (*m*, 8H, CH_2), 6.85 (*d*, 2H, CH), 6.91 (*d*, 1H, CH), 7.39 (*d*, 2H, CH), 7.58 (*d*, 1H, CH), 7.69 (*s*, 1H, CH)		[a]
22b (**ABC**)	582 (4.50)	3.33 (*t*, 4H, CH_2), 3.64 (*t*, 4H, CH_2), 3.75 (*m*, 8H, CH_2), 3.81–3.86 (*m*, 8H, CH_2), 6.92 (*d*, 1H, CH), 7.09 (*d*, 2H, CH), 7.34 (*d*, 2H, CH), 7.55 (*d*, 1H, CH), 7.66 (*s*, 1H, CH)	46.67, 48,36, 51.87, 65.08, 65.68, 66.17, 113.42, 124.99, 126.16, 131.33, 132.95, 133.41, 148.27, 152.88, 168.29, 175.58, 177.62, 179.56	[a]
23a (**bCC**)	591 (4.45)	3.45 (*s*, 6H, CH_3), 3.61 (*t*, 8H, CH_2), 3.75 (*t*, 8H, CH_2), 7.21 (*d*, 1H, CH), 7.82 (*s*, 2H, CH), 8.07 (*d*, 1H, CH)	43.90, 48.14, 65.01, 108.66, 119.29, 122.59, 128.48, 146.67, 150.65, 174.66, 177.55	[a]
23b (**BCC**)	600 (4.44)	3.64 (*m*, 8H, CH_2), 3.75 (*m*, 8H, CH_2), 3.84 (*m*, 8H, CH_2), 7.30 (*d*, 1H, CH), 7.87 (*s*, 2H, CH), 8.12 *d*, 1H, CH)	48.30, 51.80, 65.15, 104.54, 118.18, 122.82, 127.51, 147.58, 151.66, 175.05, 176.72	[a]
24a (**aCC**)	545 (4.66)	3.16 (*s*, 6H, CH_3), 3.19 (*t*, 8H, CH_2), 3.79 (*t*, 8H, CH_2), 6.94 (*d*, 2H, CH), 7.58 (*d*, 2H, CH), 8.14 *s*, 2H, CH)	40.05, 50.60, 65.58, 111.98, 125.49, 132.03, 134.10, 147.32, 152.99, 153.41, 172.25	[a]
24b (**ACC**)	558 (4.24)	3.25 (*t*, 4H, CH_2), 3.76 (*t*, 8H, CH_2), 3.80–3.82 (*m*, 12H, CH_2), 7.31 (*d*, 2H, CH), 7.58 (*d*, 2H, CH), 8.18 (*s*, 2H, CH)	46.37, 49.36, 65.06, 65.60, 113.40, 125.07, 126.99, 134.79, 154.29, 161.65, 169.28, 178.28	[a]

(*continued on next page*)

Table 2 (*continued*)

Comp (code)[a]	λ_{max} (log ε) [nm] in MC	^{1}H NMR, δ-values in ppm	^{13}C NMR δ-values in ppm	Solvent[b]
25b (**CCC**)	570 (4.42)	3.78 (*m*, 24H, CH_2), 8.35 (*s*, 3H, CH)	49.05, 65.15, 104.54, 124.64, 158.89, 177.21	[a]
40 (**NSS**)	617 (4.89)	2.89 (*s*, 6H, SCH_3), 3.80 (*s*, 3H, $N(CH_3)_2$), 7.39 (*d*, 2H, CH), 7.72–7.73 (*m*, 3H, CH), 8.26 (*d*, 1H, CH)	17.97, 43.38, 127.77, 127.98, 131.91, 137.32, 138.82, 142.25, 148.78, 153.65, 181.56	[b]
41 (**SSS**)	614 (4.89)	3.04 (*s*, 9H, SCH_3), 7.63 (*d*, 3H, CH), 8.14 (*d*, 1H, CH)	17.17, 129.01, 138.70, 144.02, 149.08, 171.78	[b]
42 (**HSS**)	620 (4.86)	3.08 (*s*, 6H, SCH_3), 7.69 (*d*, 2H, CH), 7.75 (*t*, 1H, CH), 8.12 (*d*, 1H, CH), 8.24 (*d*, 2H, CH), 8.50 (*d*, 1H, CH)	17.32, 129.95, 130.53, 139.70, 140.19, 140.87, 141.42, 145.90, 151.37, 177.65	[b]
43 (**HHN**)	483 (4.30) 388 (3.95)	3.59 (*s*, 3H, $N(CH_3)_2$), 3.70 (*s*, 3H, $N(CH_3)_2$), 7.24–7.27 (*m*, 2H, CH), 7.35 (*d*, 1H, CH), 7.41 (*d*, 1H, CH), 7.61 (*d*, 1H, CH), 7.76 (*d*, 1H, CH), 7.79 (*d*, 1H, CH), 7.94 (*d*, 1H, CH)	45.09, 47.28, 124.79, 129.29, 129.75, 134.23, 135.21, 135.79, 136.60, 149.70, 183.03	[c]
44 (**HHH**)	472 (4.55) 367 (3.69)	8.03 (*m*, 3H, CH), 8.49 (*m*, 3H, CH), 9.11 (*m*, 3H, CH) CH)	133.38, 142.82, 147.36, 152.68, 164.60	[b]
45 (**HNN**)	618 (4.84)	3.32 (*s*, 12H, $N(CH_3)_2$), 6.77 (*d*, 2H, CH), 7.32 (*t*, 1H, CH), 7.50 (*d*, 1H, CH), 7.62 (*d*, 2H, CH), 8.02 (*d*, 1H, CH)	42.77, 112.59, 124.40, 127.79, 131.85, 133.29, 138.19, 139.81, 144.35, 173.64	[a]
46 (**NNS**)	562 (4.40)	2.65 (*s*, 3H, SCH_3), 3.31 (*s*, 12H, $N(CH_3)_2$), 6.77 (*d*, 2H, CH), 7.26 (*d*, 1H, CH), 7.42 (*d*, 1H, CH), 7.68 (*d*, 2H, CH)	19.12, 42.74, 112.49, 123.99, 128.08, 134.43, 137.63, 144.18, 144.22, 146.05, 173.43	[a]
47 (**HHS**)	565 (4.62)	2.46 (*s*, 3H, SCH_3), 6.78 (*d*, 1H, CH), 6.93–6.98 (*m*, 4H, CH), 7.25 (*d*, 1H, CH), 7.44 (*d*, 2H, CH)	17.95, 131.15, 132.09, 141.01, 141.16, 142.45, 144.26, 148.57, 154.79, 188.63	[a]
48 (**HNS**)	541 431	2.63 (*s*, 3H, SCH_3), 3.53 (*s*, 6H, $N(CH_3)_2$), 7.05 (*t*, 1H, CH), 7.21-7.24 (*m*, 2H, CH), 7.29 (*d*, 1H, CH), 7.37 (*d*, 1H, CH), 7.46 (*d*, 1H, CH), 7.74 (*d*, 1H, CH), 7.79 (*d*, 1H, CH)		[c]

[a] Depiction of the type of attached aromatic rings, or substitution pattern, in the dye perchlorate; for the meanings of the letters, see Schemes 1–6.

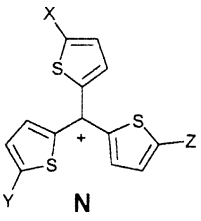
[b] NMR solvent: [a] DMSO-D6, [b] CF3COOD, [c] CDCl3.

several trityl compounds the studied molecules exist in a propeller-shaped configuration their side groups have tilde-angles which depend on the type of side group (phenyl or thienyl) and on their substitution pattern. To adapt this molecular distortion in the calculations the resonance integral β_{ab} between the central methine C-atom and its side groups was reduced with respect to the other resonance integrals β_{CC} according to the relationship $\beta_{ab} = 0.7\ \beta_{CC}$. The other parameters used for the calculations were those described in the literature [29].

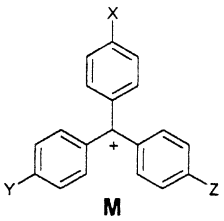
As can be seen from Table 3 in which the calculated data are compared with experimental data, the PPP-calculations reproduce the spectral properties of the studied compound very well. Thus, the strong bathochromic shift of the longest-wavelength absorption band on going from the unsubstituted parent compounds to their dimethylamino or methylmercapto substituted derivatives is

Table 3
Measured and by means of the PPP method calculated UV/vis spectral data of several tris-(thienyl)methinium ions and their corresponding carbocyclic analogues

Substituents



N



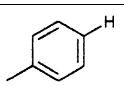
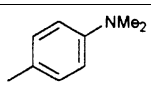
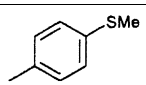
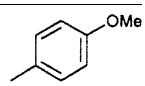
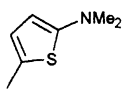
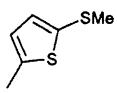
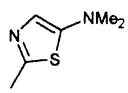
M

X	Y	Z	Comp.	λ_{max}(found) [nm]	(log ε)	λ_{max}(calc) [nm]	(log f)	Comp.	λ_{max}(found) [nm]	(log ε)	Ref.	λ_{max}(calc) [nm]	(log f)
H	H	H	**44**	472	(4.55)	488	0.560	**49**	432	(4.57)	[27]	462	0.003
						487	0.561					454	0.006
				367	(3.69)	428	0.001					454	0.006
N	H	H	**43**	483	(4.30)	548	0.913	**50**	490	(4.05)	[27]	519	1.019
						456	0.449					410	0.001
						392	0.013					410	0.030
N	N	H	**45**	618	(4.86)	614	0.934	**51**	620	(4.66)	[27]	594	1.066
						476	0.518					443	0.455
						368	0.037					379	0.019
N	N	N	**19a**	607	(4.89)	598	0.700	**7a**	590	(5.00)	[27]	571	0.901
						598	0.790					571	0.902
				334	(4.26)	356	0.001					367	0.000
S	S	S	**41**	614	(4.89)	606	0.692	**52**	586	(4.98)	[27]	595	0.746
						605	0.692					594	0.747
						385	0.000					413	0.000
S	S	H	**42**	620	(4.86)	622	0.776	**53**	594	(4.98)	[27]	615	0.845
						502	0.483					483	0.376
						392	0.031					407	0.021
S	H	H	**47**	565	(4.62)	569	0.734	**54**	547	(4.71)	[27]	554	0.748
						471	0.488					431	0.002
						405	0.017					427	0.039

very closely reproduced. The same is true for the observed bathochromic or hypsochromic shifts on going from the mono-substituted derivatives to the di- and tri-substituted derivatives in the trityl as well as in the tris(thienyl)methinium series. Furthermore, the strong bathochromic effect of a methylmercapto group, which is nearly the same as that provide by a dialkylamino group, is very well reproduced.

At first glance this fact seems surprising because the longest-wavelength absorptions in the methylmercapto- and dimethylamino-substituted trityl and tris(thienyl)methinium compounds have a strong charge-transfer character resulting from electronic excitation from the substituted (het)aryl moieties to the central, electron-accepting methine group, and should therefore be controlled by the ionisation potential of the donor moiety and the electron affinity of the acceptor moiety, and a methylmercapto group is a much more weaker electron donor than a dialkylamino group according to their Hammett σ_p-values ($\sigma_p(SMe) = -0.047$; $\sigma_p(NMe_2) = -0.60$) [30]. Thus one might expect λ_{max} of a dimethylamino-substituted trityl or tris(2-thienyl)methinium compound to occur at longer wavelengths than the λ_{max} of the methylmercapto-substituted compounds with the same substitution pattern. This statement is supported by considering the ionisation potentials of the appropriate (het)aryl groups linked at the central

Table 4
Calculated ionisation potentials of different side groups used as building blocks in tris-(thienyl)methinium salts (upper part) and ionisation energies and electron affinities of these groups in a C_3-arrangement around a central methinium ion (lower part)

moiety				
abbreviation	$\mathbf{H_A}$	$\mathbf{N_A}$	$\mathbf{S_A}$	$\mathbf{O_A}$
$\mathbf{I}\mathbb{P}_1$ [eV]	10.661	8.495	8.897	9.424
$\mathbf{I}\mathbb{P}_2$ [eV]	13.576	10.337	10.493	10.463
moiety				
abbreviation	$\mathbf{H_A}$	$\mathbf{N_A}$	$\mathbf{S_A}$	$\mathbf{O_A}$
$\mathbf{I}\mathbb{P}_1$ [eV]	9.652	7.875	8.458	8.125
$\mathbf{I}\mathbb{P}_2$ [eV]	10.159	9.804	9.981	10.110
compound				
EA [eV]	10.323	9.270	9.729	9.661
$\mathbf{I}\mathbb{P}_1$ [eV]	13.845 (3)	11.125 (3)	11.542 (3)	12.293 (3)
$\mathbf{I}\mathbb{P}_2$ [eV]	13.845 (3)	11.125 (3)	11.542 (3)	12.293 (3)
$\Delta E_{(\mathbb{P}_1-EA)}$	3.522	1.855	1.813	2.632
compound				
EA [eV]	10.354	9.246	9.742	9.643
$\mathbf{I}\mathbb{P}_1$ [eV]	13.288 (3)	10.804 (3)	11.367 (3)	11.778 (3)
$\mathbf{I}\mathbb{P}_2$ [eV]	13.648 (3)	12.819 (3)	13.157 (3)	13.135 (3)
$\Delta E_{(\mathbb{P}_1-EA)}$	2.934	1.558	1.625	2.135

methine group calculated by means of the PPP method.

As can be seen from Table 4, the calculated data indicates a difference between the ionisation potentials (IP) of the dimethylamino- and methylmercapto-substituted benzene and thiophene compounds of 0.492 and 0.583 eV, respectively. These differences are significantly diminished, namely to +0.153 eV and −0.146 eV, respectively, if the appropriate CT-energies are calculated assuming that they originate by electronic excitation from the (het)aryl moieties to the central methine group arranged between the three (het)aryl moieties in a C_3 symmetry, and neglecting the corresponding resonance integrals between these moieties. This decrease is obviously caused by the neighbouring strongly electron accepting, positively charged methine group as well as by the changes in the electron repulsions within the appropriate (het)aryl moieties. Hence, the strong similarity in the spectral properties of dialkylamino- and alkylmercapto-substituted trityl and tris(2-thienyl)methinium compounds results from a compensation of the effects originating from differences in the ionisation potentials and the electron repulsion of the appropriate (het)aryl moieties.

The observed spectral effects on going from the unsubstituted trityl or tris(2-thienyl)methinium parent compounds, designated as H_3C^+, to their mono-, bis-, and tris-substituted derivatives, designated as H_2XC^+, HX_2C^+, and X_3C^+, respectively, can also be qualitatively explained theoretically. For this, the data of Fig. 1 are helpful. Thus the charge-transfer transitions **T** discussed before and resulting from electronic excitation from an attached aromatic ring to the central electron-accepting methine moiety are

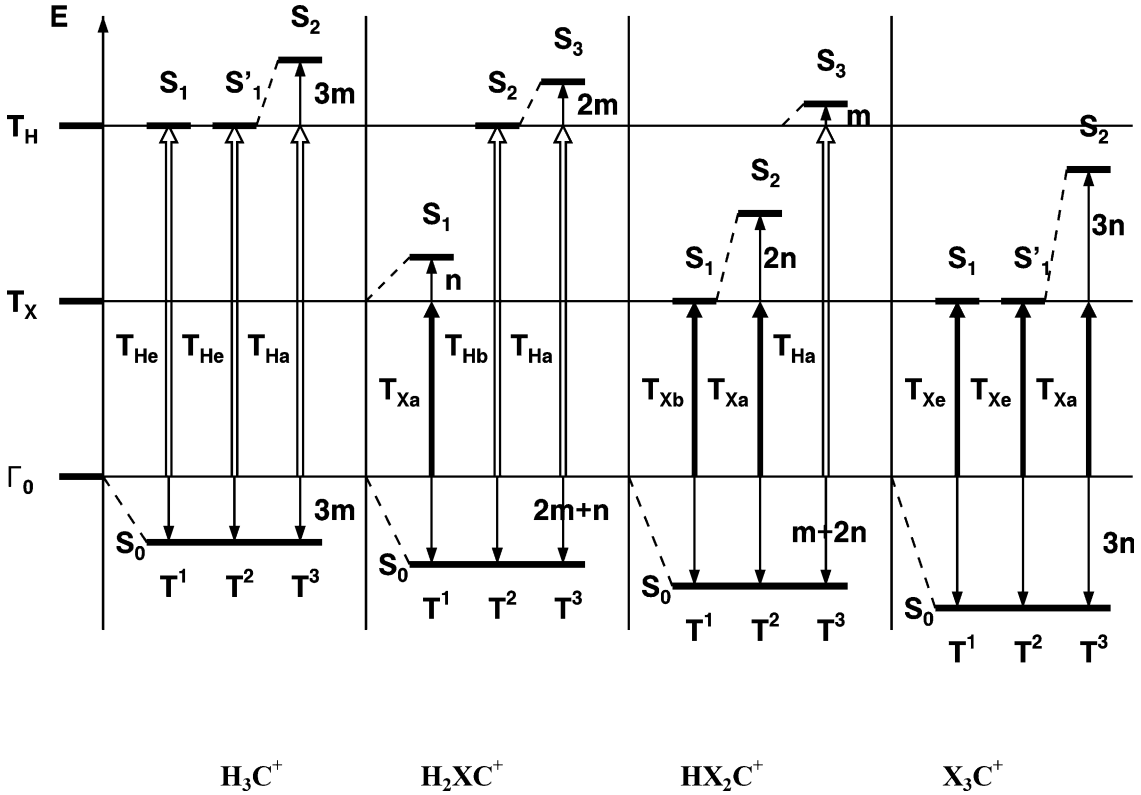


Fig. 1. Results for configuration interaction by coupling tri (het)aryl moieties in a C3-arrangement with a central methine moiety; the symbols H and X represent an unsubstituted or substituted (het)aryl moiety, respectively; for the meaning of the other symbols see text.

shown for compounds with different types of substitution pattern. As can be seen, in the unsubstituted parent compound H_3C^+, assuming that there is no electronic coupling between the attached rings and the central moiety, there are, in addition to the so-called non-bound ground configuration Γ_0, three electronic transitions, named as T_H, which split, due to the assumed C_3 symmetry of the molecules, into two $\mathbf{T_{He}}$ and one $\mathbf{T_{Ha}}$ transitions [31]. In the mono-substituted compound H_2XC^+, assumed to have a C_2 symmetry, there are two $\mathbf{T_H}$ transitions, split by symmetry into a $\mathbf{T_{Ha}}$ and a $\mathbf{T_{Hb}}$ transition, and one $\mathbf{T_{Xa}}$ transition. In the bis-substituted compound HX_2C^+, also assuming a C_2 symmetry, there are two $\mathbf{T_X}$ transitions, split by symmetry into a $\mathbf{T_{Xa}}$ and a $\mathbf{T_{Xb}}$ transition, and a $\mathbf{T_{Ha}}$ transition. Finally, in the tris-substituted compound X_3C^+ with a C_3 symmetry there are three $\mathbf{T_X}$ transition which split by symmetry into two $\mathbf{T_{Xe}}$ transitions and one $\mathbf{T_{Xa}}$ transition.

In the case of coupling of the attached aromatic rings groups with the central methine moiety a mixing of configurations occurs. As result of this mixing some of the transitions become changed in energy. The energy change depends on the symmetry of the molecules and can be calculated, in a row approximation, by means of a perturbation treatment. Thus, each of the $\mathbf{T_H}$ and $\mathbf{T_X}$ transitions gives rise to an energetic stabilisation m and n of the non-bound ground configuration and to an energetic destabilisation of the excited configuration of $-m$ and $-n$, respectively. Their multipliers depend, as depicted in Fig. 1, on the symmetry of the molecules and their values can be calculated by means of Eq. 1. Thus, in the C_3-molecules H_3C^+ and X_3C^+ there is an energy stabilisation of the non-bound configuration of 3m and 3n, respectively, whereas only one of their charge-transfer configurations ($\mathbf{T_{Ha}}$ and $\mathbf{T_{Xa}}$) is destabilised by the same amount. Hence, in both these molecules the longest-wavelength transitions ($\mathbf{T_1}$ and $\mathbf{T_2}$) are energetically degenerate, whereas the third electronic transition ($\mathbf{T_3}$) is raised by $-3m$ or $-3n$, respectively.

$$m = \frac{H^2_{\Gamma T_H}}{E_{T_H}}; \qquad n = \frac{H^2_{\Gamma T_X}}{E_{T_X}} \tag{1}$$

In the molecules H_2XC^+ and HX_2C^+ having a C_2-symmetry there is a stabilisation of their non-bound configuration of $2m+n$ and $m+2n$, respectively, whereas two of their excited configurations, $\mathbf{T_{Ha}}$ and $\mathbf{T_{Xa}}$, are destabilised by $-2m$ and $-n$ in the mono-substituted compound H_2XC^+ and by $-m$ and $-2n$ in the bis-substituted compound HX_2C^+. Hence, in both of these molecules the longest wavelength transitions $\mathbf{T_1}$–$\mathbf{T_3}$ are split into three transitions, each of different energy. Due to the fact that $E(\mathbf{T_X}) < E(\mathbf{T_H})$, the relationship $m < n$ holds, and thus the unsubstituted parent compound H_3C^+ must absorb at shorter wavelength than the mono-substituted compound H_2XC^+. Similarly the latter compound must absorb at shorter wavelength than the bis-substituted compound HX_2C^+. In turn, this compound must absorb at longer wavelength than the tris-substiuted compound X_3C^+, irrespective of which series of compounds is considered (e.g. the trityl or the tris(2-thienyl)methinium series), and this is in accord with the experimental observations.

3. Experimental

3.1. General

Melting points were determined by means of a Boetius heating-table microscope and are corrected. The UV/vis spectra were recorded with a MC 400 spectrometer (Zeiss, Jena, Germany), and the NMR spectra with a 300 MHz spectrometer Gemini 300 (Varian, Zurich, Switzerland). The elemental analysis were dertermined with a CHNS analyser 932 (LECO, USA).

The *N,N*-disubstituted 2-aminothiophenes **2** [2b], 2-aminothiazoles **3** [7,10a], and 2-methylmercaptothiophene **34** [32] used as starting materials for the preparation of the corresponding lithium derivatives **38** and **35**, respectively, were prepared accordingly to reported procedures. The *N,N*-disubstituted 2-aminothiophene-5-carboxylates **12** [22], 2-aminothiazole-5-carboxylates **15** [33], 2-amino-5-chloroacetylthiophenes **13** [24], and 2-amino-5-chloracetylthiophenes **14** [24] were prepared accordingly to the given literature.

3.2. Preparation of 5-dimethylamino-bis(2-thienyl)ketone **29**

After refluxing a mixture of *N,N*-tetramethyl-3-anminothioacrylamide (**9**, R=CH_3, 0.01 mol) and 2-bromoacetylthiophene (0.01 mol, 2.0 g) in acetonitrile (50 ml) for 10 min triethylamine (10 ml) was added. The mixture was cooled to room temperature and acidified with aqueous acetic acid (50 ml, 25%). The product crystallised out and was isolated by filtration, dried in air, and recrystallised from *n*-butanol. ^{1}H NMR, δ-values (in $CDCl_3$): 3.10 (s, 6H, NCH_3), 5.93 (*d*, 1H, CH), 7.12 (*dd*, 1H, CH), 7.55 (*d*, 1H, CH), 7.73 (*d*, 1H, CH), 7.75 (*d*, 1H, CH).

3.3. Preparation of 5-methylmercaptothiophene-2-carboxylic acid **36**

To a solution of 2-methylmercaptothiophene **34** [32] (0.03 mol, 3.9 g) in dried dioxane (20 ml) lithium butyl (0.09 mol) in hexane (1.6 M) was added under argon at −10 °C. After 30 min carbon dioxide was bubbled into the reaction mixture for 30 min. Then the mixture was refluxed for 8 h, cooled to room temperature, poured in water (300 ml), and acidified with acetic acid (20 ml). The thiophene-2-carboxylic acid formed was isolated by filtration, dried in vacuo at room temperature and used without further purification. Yield 30%; mp 104–105 °C. ^{1}H NMR, δ-values (in $CDCl_3$): 2.60 (*s*, 3H, SCH_3), 6.94 (*d*, 1H, CH), 7.73 (*d*, 1H, CH).

3.4. Preparation of methyl 5-methylmercaptothiophene-2-carboxylate **37**

The previously prepared 5-methylmercaptothiophene-2-carboxylic acid **36** (0.01 mol, 1.75 g) was mixed with thionyl chloride (10 ml) and refluxed for 3 h. After evaporation of the reaction mixture, methanol (10 ml) was added with stirring and cooling at room temperature. The mixture was concentrated in vacuo and the residue was purified on silica by elution with dichloromethane. The brown oil obtained was used without further purification. ^{1}H NMR, δ-values (in $CDCl_3$): 2.56 (*s*, 3H, SCH_3), 3.85 (*s*, 3H, OCH_3), 6.92 (*d*, 1H, CH), 7.63 (*d*, 1H, CH).

3.5. Preparation of heterocyclic triphenylmethinium derivatives—general procedure

3.5.1. Method A

The heterocyclic ketone **16–18** (0.004 mol) and the appropriate *N,N*-disubstituted amine **1–3** (0.02 mol) in phosphorylchloride (5 ml) were refluxed for 3 h. After cooling the reaction mixture was poured in ethyl acetate (15 ml) containing perchloric acid (1 ml, 70%). The resultant precipitate was isolated by filtration, washed with ethyl acetate or diethyl ether, and recrystallised from acetic acid. The compounds prepared are summarised in Table 1.

3.5.2. Method B

The *N,N*-disubstituted heterocyclic amine **1–3**, **30**, or **34** (0.01 mol) was dissolved under argon in dry 1,4-dioxane (15 ml) and cooled to −15 °C. Lithium butyl (0.03 mol), dissolved in *n*-hexane (1.6 M), was slowly added with stirring and cooling, when the lithiated compound precipitated as a white solid. After stirring for 10 min at 0 °C, the relevant methyl carboxylate **12**, **15**, **33**, or **37** (0.005 mol), or ketone **16–18** or **29** (0.005 mol), or dimethyl carbonate **28** (0.003 mol), was added. The resulting mixture was slowly warmed to room temperature and then refluxed for 8 h. After cooling to room temperature and filtering, aqueous perchloric acid (2 ml, 70%) was added with stirring. The resultant precipitate was isolated, washed with diethyl ether, and recrystallised from acetic acid or DMF. The compounds prepared are listed in Table 1.

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