Structural properties and ¹³C chemical shifts of bis- and tris(2-thienyl)methinium and related cations: a combined theoretical and experimental study†

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epoc ABSTRACT: The molecular structure of the parent bis- and tris(2-thienyl)methinium ions were studied by first-principles methods (second-order Møller–Plesset many-body perturbation theory and density functional theory). In contrast to bis(2-thienyl)methinium, tris(2-thienyl)methinium is non-planar with torsion angles between the thienyl groups and the central plane of about 30°. The calculations on tris(2-thienyl)methinium resulted in two almost isoenergetic conformers with barriers to isomerization less than 10 kcal mol^{-1} (1 kcal = 4.184 kJ). In order to discuss the ^{13}C chemical shifts of Crystal Violet and of heteroanalogous compounds with thienyl-2-, with 5-amino-thienyl-2-, with 5-methylmercapto-thienyl-2- and with 5-amino-1,3-thiazolyl-2-heteroaryl groups, the structure was optimized at the DFT B3-LYP/6–31G(d) level and the chemical shifts were calculated at the DFT-GIAO/6–311 + G(2d,p) level of theory. In general, the experimental chemical shifts correlate very well with the experimental values. The lowest energy electronic transitions in the UV–VIS region were calculated by time-dependent density functional response theory (TD-DFRT) using the DFT B3-LYP/6–31 + G(d) basis set. For cationic dyes the agreement between the results of TD-DFRT calculations and experiment was less good than for neutral sulfur-containing compounds. Semiempirical calculations (PPP, ZINDO/S) are better in that case and are more efficient. Copyright © 2002 Wiley & Sons, Ltd.

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KEYWORDS: tris(2-thienyl)methinium ions; molecular structure; ^{13}C NMR chemical shifts; UV–VIS spectral data; quantum chemical calculations

INTRODUCTION

The heterocycles **1** and **2** are the parent compounds of a series of cationic dyes. Novel heterocyclic analogues of the well-known Crystal Violet chromophore **3** such as tris(5-donor-substituted-2-thienyl)methinium compounds **4** and their aza analogues **5** have been prepared recently and characterized spectroscopically.[1] In analogy with its carbocyclic counterparts,[2] sulfur-containing compounds are deeply coloured with intense absorption maxima at about 600 nm. Less is known about the structures of these compounds. Two different structures **A** and **B** may be anticipated for bis(2-thienyl)methinium (**1**) and tris(2-thienyl)methinium (**2**). Studies on the structure by MMX[3] and MM2[1] force field methods did not give a uniform answer about the isomers. X-ray diffraction analysis of tris(2-thienyl)methinium (**2**) per-
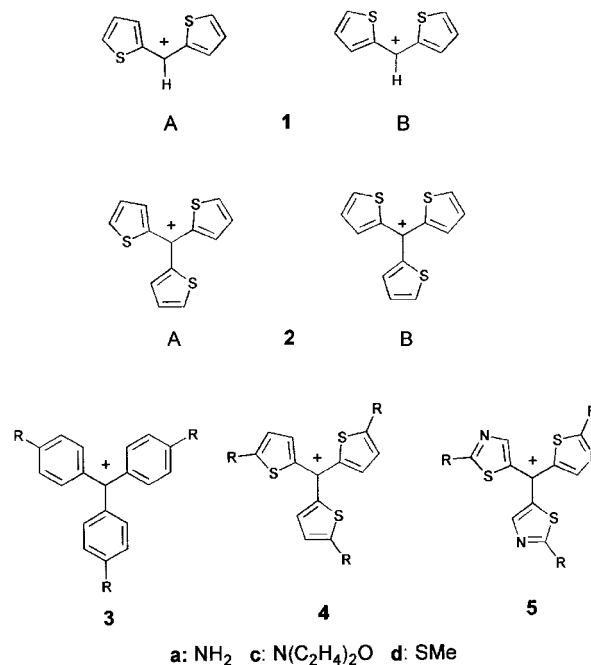
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†Dedicated to Professor Roland Mayer on the occasion of his 75th birthday.

chlorate revealed a structure of low symmetry, closer to **A** than to **B**.[3] Triphenylmethinium dyes of the series **3** display a propeller-shaped structure in the crystal.[4] The structure of **3** was also discussed theoretically by INDO calculations.[5] Additional, more recent information is available with ^{13}C chemical shifts of dyes of the series **4** and **5**.[1] To the best of our knowledge, first-principles methods have not yet been employed in the study of the structures and properties of triheteroarylmethinium ions.

The aim of this study was twofold: first, to define the molecular structure of the parent compounds **1** and **2** by post-Hartree–Fock *ab initio* quantum chemistry and, more generally, by density functional theory (DFT); and second, to calculate and to interpret experimental NMR and UV–VIS spectral data for bis(2-thienyl)methinium (**1**), tris(2-thienyl)methinium (**2**) and the derivatives **4** and **5** by DFT-based methods.

COMPUTATIONAL

The study was based on the Hohenberg–Kohn–Sham density functional theory (DFT).[6] The hybrid HF/DF exchange functional defined by Becke's three-parameter equation[7] was employed throughout this study. It was used in conjunction with the Lee–Yang–Parr correlation functional[8] and, in some test calculations, with the Perdew 98 functional,[9] denoted B3-LYP and B3-P89, respectively. Whereas molecular geometries were calculated mainly by means of the polarized split-valence double-zeta basis set 6–31G(d) (VDZ, for short), the more extended valence triple-zeta basis set 6–311 + G(2d,p) (VTZ) was used in calculating magnetic shielding constants σ by the 'gauge-independent atomic orbital' (GIAO) method.[10,11] NMR ^{13}C chemical shifts δ were obtained by subtracting the calculated magnetic shielding σ of the carbon nuclei from the shielding of carbon of the reference compound (tetramethylsilane, $\sigma_0 = 183.35$ ppm).

The molecular geometries were fully optimized. The stationary points on the DFT energy surface were characterized as local minima and transition structures by the number of negative eigenvalues of the Hessian matrix (zero or one, respectively). A single imaginary frequency defines the transition structure. In search of transition structures the tight optimization convergence criterion was used (opt = tight). The good performance of DFT in calculating relative energies and molecular geometries was confirmed by second-order many-body perturbation theory (MBPT2) calculations, commonly denoted as Møller–Plesset perturbation theory calculations (MP2).[12] The outcome of MP2(fc)/6–31G(d) calculations in this study justifies the application of the computationally less demanding DFT B3-LYP/6–31G(d) model for the whole series of triheteroarylmethinium compounds. DFT electron densities were computed from SCF con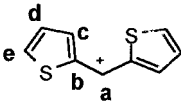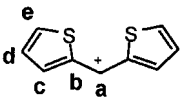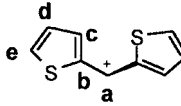verged Kohn–Sham orbitals. Total charges were defined by the traditional Mulliken analysis or by natural population analysis.[13] The natural population analysis provides atomic charges based on occupancies of the orthonormal natural atomic orbitals on each center.

Because of the large computational expenditure in calculating UV–VIS spectral features by high level correlated *ab initio* methods organic compounds were preferably studied by semiempirical methods.[14] These methods are single-reference-based (SCF-CI), usually taking singly excited configurations only into account (CIS). The empirically scaled ZINDO/S method was spectroscopically parameterized for a few important elements of the periodic table. However, the method is not devoid of shortcomings. Thus, less satisfactory results were obtained for sulfur-organic compounds and the method failed entirely with some low-energy colour-determining transitions.[15] Since multi-reference-based *ab initio* methods[16] are prohibitive for the compounds of larger size, time-dependent density functional theory may be considered as an alternative. In contrast to ZINDO/S, this method is a first-principles method, i.e. this method needs no parameterization in excited-state calculations. Moreover, the method is easily applicable for additional main group elements of the periodic table. In calculating sulfur-organic compounds, TD-DFT performs definitely better than ZINDO/S.[15] However, erratic cases were also found with TD-DFT. To test the scope and limitations of the methods, more complex dye chromophores such as tri(2-thienyl)methinium and related ions were calculated in this study.

The TD-DFRT calculation of the excitation energies is done in two steps:[6,17] first, SCF-DFT calculation of the single-particle Kohn–Sham orbitals and the corresponding energies, and second, calculation of the excitation energies. More specifically, the frequency-dependent linear response (R) of the electron densities is studied with respect to an external field that is a time-dependent perturbation. The dynamic polarizability describes the response of the dipole moment to a time-dependent electrical field. The polarizability diverges for definite frequencies. It has poles at the electronic excitation energies. This calculation also provides the oscillator strengths of the respective electronic transitions. The TD-DFRT approach differs basically from SCF-CI method, such as ZINDO/S. The first-mentioned method is transition oriented whereas the latter is state oriented. The TD-DFRT transition energy is defined in terms of ground-state properties. The calculations were performed, in turn, with B3-LYP functionals. Since transition energies are less sensitive to the basis set, 6–31 + G* is sufficient and was used in all TD-DFRT calculations.

TD-DFRT differs grossly from ZINDO/S in computer time. ZINDO/S approximately scales with N^1. Scaling amounts to N^3 in the present implementation of TD-DFRT. Two aspects, however, are in common for the two different approaches: first, in contrast to the high-level correlated *ab initio* calculations they are not dependent

Table 1. Selected bond lengths of planar dis(2-thienyl)methinium (**1**) isomers and the non-planar transition structure of the *trans*-to-*cis* isomerization in Å calculated by different theoretical models[a,b] (ΔE and $\Delta E^{\neq}$ are relative energies with respect to the *trans* conformer; bond lengths in Å and relative energies in kcal mol^{-1})

Bond	*trans*				*cis*				TS (*cis–trans*)[c]			
	LYP VDZ	LYP VTZ	P86 VDZ	MP2 VTZ	LYP VDZ	LYP VTZ	P86 VDZ	MP2 VTZ	LYP VDZ	LYP VTZ	P86 VDZ	MP2 VTZ
a–b	1.401	1.395	1.397	1.400	1.399	1.394	1.395	1.398	1.364	1.357	1.362	1.368
b–c	1.411	1.406	1.408	1.416	1.411	1.407	1.408	1.416	1.432	1.428	1.428	1.432
c–d	1.397	1.391	1.393	1.390	1.397	1.391	1.393	1.390	1.380	1.373	1.373	1.376
d–e	1.387	1.382	1.385	1.394	1.387	1.383	1.385	1.395	1.408	1.404	1.404	1.416
S–b	1.764	1.757	1.751	1.738	1.766	1.759	1.753	1.741	1.782	1.777	1.769	1.758
S–e	1.714	1.706	1.703	1.700	1.713	1.705	1.702	1.700	1.694	1.685	1.685	1.677
$\Delta E/\Delta E^{\neq}$	0.0	0.0	0.0	0.0	−1.1	−0.9	−1.2	−1.5	20.1	22.2	20.0	17.4

[a] Becke's three parameter hybrid functional (B3); abbreviations of the basis sets: VDZ = 6–31G(d), VTZ = 6–311 + G(2d,p).
[b] Bonds lengths of thiophene calculated by B3-LYP VDZ (MP2 VDZ): S—C 1.736 (1.718), C—C (essentially double bonds) 1.367 (1.376), C—C (essentially single bond) 1.430 (1.420) Å.
[c] Imaginary frequencies: TS (LYP) 269 cm^{-1}, TS (P86) 266 cm^{-1}.

on sophisticated considerations in performing the calculations, and may be rather considered as 'black box' procedures, and second, the transitions in both methods can be interpreted in terms of single-electron excitations. The electron excitations are defined by the molecular orbitals that are either Kohn–Sham orbitals, in the case of TD-DFT, or Hartree–Fock orbitals, in of the case of SCF-CI (e.g. ZINDO/S).

The quantum chemical calculations were carried out using the 1998 release of the Gaussian suite of programs (Revision A.7).[18]

RESULTS AND DISCUSSION

Structure of the parent compounds

The structures **A** and **B** of bis(2-thienyl)methinium (**1**) turned out to be minima of the energy surface. The *cis* conformer **1A** is lower in energy. As documented in Table 1, the isomers differ in energy by less than 1.5 kcal mol^{-1} (1 kcal = 4.184 kJ). The distance between the sulfur atoms of **1B** was calculated to about 3.35 Å. Thus, the interatomic SS distance is shorter than the sum of the van der Waals radii (about 3.70 Å). Although a local stabilization effect between the sulfur atoms of the *cis* isomer cannot be excluded, the isomer **1B** is hardly energetically favoured over the *trans* isomer **1A**. The same holds for tris(2-thienyl)methinium (**2**). In the case of **1** the barrier to isomerization amounts to less than 25 kcal mol^{-1}. Structure and energetics are nearly independent of the theoretical model. Selected bond lengths of bis(2-thienyl)methinium (**1**) are given in Table 1.

Because the electrons of the thienyl groups are delocalized over the whole cation structure, the bond lengths of **1** differ significantly from those of the free thiophene when calculated at the same level of theory (cf. footnote in Table 1). The cation **1** displays a longer 1–2 bond (S–b, in Table 1) and a shorter 1–5 bond (S–e) bond relative to the bonds of thiophene. In addition, the CC bond 3–4 (c–d) is shortened and the carbon–carbon bonds 2–3 (b–c) and 4–5 (e–d) are elongated. The CC bonds of the thienyl ring and the central CC bonds are comparable in length to aromatic CC bonds (about 1.40 Å).

As is well known,[19] CS bond lengths are overestimated in DFT calculations. The results of MP2 B3-LYP/6–31G(d) calculations with the same basis set are more accurate for thiophene and for other sulfur-containing heterocycles. For example, the MP2 CS bond length of 1.718 Å of thiophene corresponds to an experimental bond length of 1.716 Å in the gas phase (average of ED and MW data[20]), whereas the DFT B3-LYP CS bond is considerably larger (1.736 Å). The error is reduced when DFT calculations are performed with a more extended basis set, e.g. 6–311 + G(2d,p) (VTZ), or with an exchange correction defined by P86.[21] Apart from the CS bonds, the bond lengths are nearly the same in the different theoretical models. The relative energies of the isomers in this study were also not very sensitive to the molecular structure. Satisfactory results were obtained by the less computationally demanding DFT B3-LYP/6–31 + G(d) (VDZ) model. Therefore, the calculations of the structure of the more complex cationic dyes were exclusively performed by the last-mentioned theoretical model.

According to the MP2 and DFT calculations, the isomeric bis(2-thienyl)methinium ions **1A** and **1B** are fully planar and of C_s and C_{2v} symmetry, respectively. By

Table 2. Selected bond lengths in Å and SCCC dihedral angles in degrees of tris(2-trithienyl)methinium (**2**) calculated by different theoretical models[a] (ΔE and $\Delta E^{\neq}$ are relative energies with respect to the *trans* conformer in kcal mol^{-1})

Bond	propeller-like **2A**		propeller-like **2B**		perpendicular TS1[b]	perpendicular TS2[b]	planar fully planar[c]
	B3LYP	MP2	B3LYP	MP2	B3LYP	B3LYP	B3LYP
a–b	1.434	1.425	1.433	1.426	1.418	1.430	1.467
b–c	1.400	1.409	1.401	1.408	1.414	1.410	1.408
c–d	1.405	1.396	1.404	1.397	1.399	1.400	1.401
d–e	1.382	1.392	1.382	1.391	1.384	1.381	1.375
S–b	1.766	1.752	1.766	1.740	1.769	1.771	1.785
S–e	1.712	1.700	1.713	1.701	1.713	1.712	1.704
SCCC	30.3	30.5	~30.5	~31.6	4.0/87.5[d]	0.0/53.8[d]	0.0
$\Delta E/\Delta E^{\neq}$	0.0	0.0	−0.1	<−0.1	9.5	9.2	(23.9)

[a] Basis set 6–31G(d).
[b] Imaginary frequencies calculated by DFT: TS1 69 cm^{-1}, TS2 68 cm^{-1}.
[c] Three imaginary frequencies.
[d] First value, SCCC dihedral angle of the *cis*-oriented thienyl groups; second values, dihedral angle of the third thienyl group.

contrast, tris(2-thienyl)methinium displays only a planar carbenium centre (C^+C_3) and the thienyl groups are distorted out-of-plane. The question may be asked whether the distortion is correctly predicted by DFT. Theoretical studies on biphenyl and diheteroaryls led Karpfen *et al.*[22] to the conclusion that DFT underestimates torsional angle of sterically hindered bonds whereas MP2 provides more reasonable results. However, as shown in Table 2, this problem seems not to occur with the compounds under study. The angles between the thienyl groups and the central C^+C_3 plane of **2A** calculated by DFT and MP2 are practically the same (30.3 and 30.5°, respectively). Hence DFT appears reliable for modelling the 3D structure of triphenyl- and triheteroarylmethyl cations.

Tris(2-thienyl)methinium (**2**) has much in common with bis(2-thienyl)methinium (**1**). This concerns both the bond length characteristics and the relative energies between the isomers. The propeller-shaped **2A** displays the axially symmetric structure with D_3 symmetry. The structure is shown in Fig. 1.

This conformer was obviously found by the MMX force field calculation.[3] The structure of the isomeric compounds is of C_1 symmetry (see Fig. 1). To distinguish conformer **2B** from the symmetrical propeller conformer **2A**, the designation 'SS-*cis*' conformer is used in the following. In principle, the SS-*cis* conformer is also propeller-like but with the sulfur atoms of two thienyl groups are turned to each other. The S⋯S distance of the sulfur atoms of these groups amount to 3.31 (DFT) and 3.30 Å (MP2), closely similar to that in the bis(2-thienyl) compound **1B**. The geometry calculated for the SS-*cis*

Propeller conformer
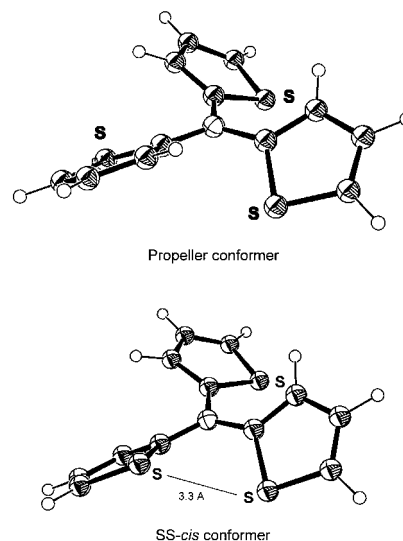
SS-*cis* conformer

Figure 1. Structures of two (2-thienyl)methinium conformers

conformer is reminiscent of a structure found in the solid state.[3] Since the structure in the crystal triaryl- and triheteroarylmethinium ions is effected by crystal forces and interaction with the counterion,[4] the agreement between the theoretical and experimental geometry should only be qualitative. The S⋯S distance in the crystal **2B** is considerably shorter (3.21 Å) than calculated. The average angles between the thiophene rings reported in experimental study amounts to 47°,[3] compared with 49° calculated by DFT. The experimental CS bond lengths are shorter than those calculated by DFT.

Two transition structures were discerned on the DFT energy surface of **2**. In both cases, two thienyl rings are coplanar in the *cis* or *trans* arrangement. In the transition structures TS1 and TS2 the third thiophene ring is situated perpendicular to one or the other planar bis(2-thienyl) substructure, respectively. The imaginary frequencies of the transition structures indicate a torsional movement of this thienyl group. The calculated barrier to torsion of **2** is less than 10 kcal mol^{-1} and hence about 10 kcal mol^{-1} lower than for **1**. Thus, compounds of the structure **2** are flexible and the isomers will efficiently equilibrate thermally at ambient temperature.

The fully planar structure **2A** of D_{3h} symmetry, however, is not a stationary point on the hypersurface. This structure has three imaginary frequencies. This compound is about 25 kcal mol^{-1} less stable than the propeller conformation (cf. Table 2). Based on an unspecified 'molecular model,' the planar structure was mistakingly assumed to be favoured over the propeller-shaped structure.[23]
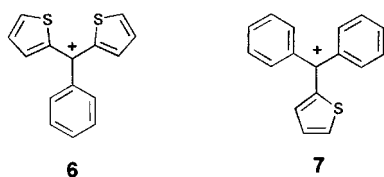
Replacement of one of the thienyl groups of **2** leads to **6**. In analogy with **2**, there are two conformers, which differ in energy by less than 0.1 kcal mol^{-1}. According to the DFT calculations, the SS-*cis* conformer of **6** exhibits an S···S distance of 3.25 Å, comparable to that of **2B** (3.31 Å). Replacement of a second thienyl group of **6** by phenyl results in **7**. Again, the molecule is propeller-like twisted. The ring dihedral angle between the two phenyl groups amounts to 62.6°. The corresponding angle calculated for triphenylmethinium **3** (R = H) is slightly smaller (56.0°), corresponding to a torsional angle of 54°, on average, in the x-ray structure.[4] The torsion of thienyl groups with respect to the plane of the central carbenium is again about 30°.

Structure of amino-substituted triheteroaryl-methinium compounds

The calculated structures of **4a** and **5a** are similar to that of tris(2-thienyl)methium (**2**). Selected geometric parameters of the amino-substituted compounds are assembled in Fig. 2. The calculated CC bond lengths are essentially smoothed out over the thienyl fragments including the amino donor groups. In accordance with the polymethine concept,[24] the electron delocalization may be related to chain-like fragment structures. In the case of **4a** these are nonamethine substructures with terminal nitrogen atoms. Amino substitution strengthens the bonds of the central carbon atoms. Again, the tris(5-amino-2-
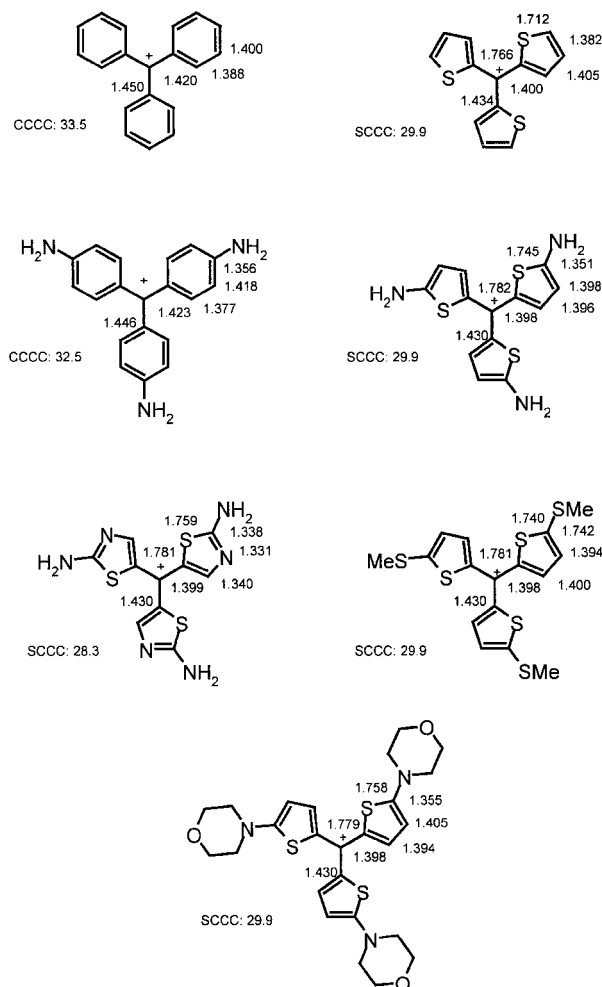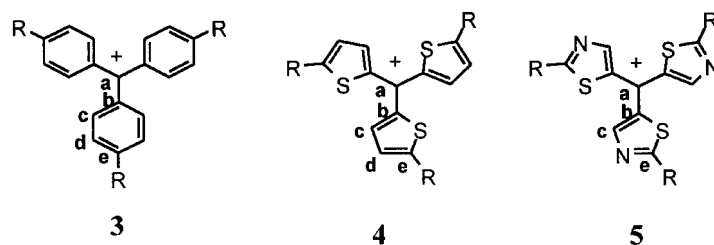

Figure 2. Selected bond lengths in Å and torsional angles in degrees relative to the central C$^+$C$_3$ plane of triphenyl and triheteroarylmethinium ions calculated at the DFT level of theory

thienyl)methinium **4a** and its aza analogue **5a** have either the symmetrical propeller-like structure or the SS-*cis*-type structure with small differences in energy (0.1 and 1.1 kcal mol^{-1}, respectively). MM2 force field calculations suggested a minimum energy structure of **4** (R = NMe$_2$) with two 5-amino-2-thienyl groups arranged in a coplanar fashion and the third one perpendicular.[1] According to DFT, this structure is a transition structure calculated to be 8.6 kcal mol^{-1} higher in energy than **2B**. Actually, the minimum energy structure is propeller-like twisted and should equilibrate at room temperature with isomeric structures.

The amino groups of **4** and **5** are slightly pyramidal in the DFT optimum structures (about 13° in the case of **4a**). A comparison between the structural data showed that the amino group is a good model for the computationally more demanding morpholino group. For that reason the morpholino group was replaced by the amino group in most calculations (cf. Table 3). For comparison crystal

Table 3. Correlation between calculated and experimental ^{13}C chemical shifts: calculated values are placed in the first line in each case and experimental values in the second line; capital letters define the type of correlation; the results of the linear regression analysis are given with the slope n, the intercept m and the correlation coefficient r

		Type of	Atomic position							Correlation[b]		
Compound	R	correlation[a]	a	b	c	d	e	Solvent	Ref.	m	n	r
3	H		212.76	147.96	150.24	137.24	152.08	—				
	H	**A**	211.6	140.6	143.3	131.1	144.1	H_2SO_4	23	−19.37	1.08	0.9994
3	NH_2		186.25	136.06	148.36	118.57	161.12	—				
	Morpholino	**B**	176.53	127.29	139.25	113.42	155.44	DMSO-d_6	1	−1.18	0.96	0.9973
3	NMe_2		186.03	134.83	146.44	117.14	162.41	—				
	Morpholino	**C**	176.53	127.29	139.25	113.42	155.44	DMSO-d_6	1	+3.17	0.93	0.9991
2	H		167.64	156.79	153.01	139.81	167.05	—				
	H[c]	**D**	153.3	132.8	137.9	124.3	143.7	H_2SO_4	23	+1.90	0.87	0.9101
	H	**D′**	164.60	142.82	147.36	133.38	152.69	CF_3COOD[c]		+5.26	0.91	0.9111
4	NH_2		154.63	138.15	149.73	115.94	181.35	—				
	Morpholino	**E**	142.29	123.23	142.38	110.18	171.02	DMSO-d_6	1	−3.05	0.95	0.9883
4	SMe		157.58	151.54	148.40	131.16	192.83	—				
	SMe	**F**	149.10	144.02	138.71	129.02	171.79	DMSO-d_6[d]		+36.91	0.70	0.9957
4	Morpholino		157.46	137.17	149.09	111.93	183.60	—				
	Morpholino	**G**	142.29	123.23	142.38	110.18	171.02	DMSO-d_6	1	+10.85	0.86	0.9828
5	NH_2		154.17	188.36	164.39	—	139.75	—				
	Morpholino	**H**	142.93	177.18	158.74	—	124.63	DMSO-d_6	23	−23.90	1.08	0.9876

[a] Pairs of calculated and experimental data under comparison (see Fig. 3). The overall correlation (**S**) of the data listed in this table is $\delta_{exp.} = -0.04\delta_{calc.} + 0.94, r = 0.9686$.
[b] $\delta_{exp.} = n\,\delta_{calc.} + m$.
[c] Assignment according to Ref. 1.
[d] A. Noack and H. Hartmann, this study.

violet **3a** was also calculated and selected structural parameters were presented in Fig. 2.

NMR chemical shifts

The ^{13}C NMR spectral shifts of morpholino-substituted triheteroarylmethinium ions reported recently[1] were not allocated to the definite carbons. A tentative assignment is given by DFT-GIAO calculations. First, experimental assignments by HMQC/HMBC 2D NMR spectroscopy were performed. The assignments of **4b** and **5b** are in perfect agreement with the theoretical prediction. The results of a more comprehensive study will be reported elsewhere (E. Kleinpeter, H. Hartmann and J. Fabian, in preparation) The experimental assignment of the chemical shifts of the parent compounds tris(2-thienyl)methinium (**2**) and triphenylmethinium (**3**) have already been published.[23]

It should be mentioned that NMR chemical shifts may be of different origin in theory and experiment. Theoretical shifts are defined for each atom of a definite

species but experimental shifts may be due more than one species equilibrating on the NMR time-scale. Fortunately, the calculated chemical shifts of the different thienyl groups of the SS-*cis* conformer are nearly the same. Actually, the chemical shifts of the corresponding carbons of the thienyl groups of the SS-*cis* conformer differ by 1 ppm on average. On the other hand, the shift values of the SS-*cis* conformer differ by less than 1.5 ppm from those of the propeller conformer. Hence the chemical shifts should hardly be effected by the presence of a equilibrium between the conformers.

Theoretical and experimental chemical shifts in the series **2–5** are given in Table 3. Experimental chemical shifts of the central carbon atoms measured in dimethyl sulfoxide are about 10 ppm lower than the calculated values. Without doubt, the large systematic error is essentially due to the solvent effect not considered in the calculations. Because of the ionic nature of the solute, the interaction with the polar solvent molecules is relatively strong. This solvent effect obviously results in an enhanced magnetic shielding of the carbon atoms. The deviation between theoretical and experimental chemical

Table 4. Charge distribution of cations **8–10** calculated by Mulliken population analysis (MPA) and natural population analysis (NPA)

Parameter	C$_6$H$_5$	CH$_2$	NH$_2$	C$_6$H$_4$	CH$_2$	NH$_2$	C$_4$H$_2$S	CH$_2$
π-Charges[a]								
MPA	0.65	0.35	0.40	0.37	0.23	0.40	0.42	0.17
Total charges[b]								
MPA	0.77	0.23	0.04	0.84	0.12	0.10	0.77	0.13
NPA	0.55	0.45	0.19	0.48	0.33	0.20	0.53	0.27

[a] Presuming a core charge of 1 for the methinium carbon and 2 for the amino-nitrogen, formal charges were calculated as 'π-charges' from the gross atomic population.

[b] The charge the hydrogen atoms were added to the charge of the adjacent non-hydrogen atoms (nitrogen or carbon).

shifts in the series **3–5** is more than twice as large as for neutral compounds calculated at the same level of theory[11] (about 4 ppm). This error is not confined to GIAO results. IGLO calculations based on *ab initio* quantum theory also predicted larger chemical shifts for simple carbenium ions than found experimentally,[25] such as for the *tert*-butyl cation measured in magic acid. The largest change in the chemical shift occurs at the central carbon. The calculated chemical shifts of the central carbons decrease in the order **3** (R = H) >**3** (R = NH$_2$) >**4** (R = H) >**4** (R = SMe) >**4** (R = NH$_2$) by 58 ppm between the first and the last compound. The decrease was experimentally found to 69 ppm. Similarly, the calculated chemical shift decreases in the order **2** >**6** >**7** by 38 ppm (experimental, 28 ppm).

It is tempting to attribute the pronounced change in chemical shift to differences in the charge distribution. Unfortunately, the charge on an atom in a molecule can neither be defined unequivocally nor is subject to experimental measurement. Regardless of this difficulty, reasonable information is gained from charges. The prototype relationship between ^{13}C chemical shifts and π-charges is known as the Spiesecke–Schneider equation found for uncharged and charged $(N + 1)\pi$ hydrocarbons,[26] where π-charges are defined by formal charges in terms of resonance structures. According to the slope of the linear relationship, one charge unit corresponds to a change in chemical shift of about 160 ppm. The 5-aminothienyl group of **4a** is expected to reduce the positive charge at the central carbenium ion more efficiently than 4-aminophenyl and, to a much larger extent, with respect to phenyl. A decrease of the charge should bring about an upfield shift at the central carbon. To calculate π-charges, the planar carbocations of benzyl (**8**), *p*-aminobenzyl (**9**) and 5-aminothienylmethyl (**10**) were considered instead of the non-planar cations **3–5**. The calculated charge distributions and the chemical shifts at the exocyclic carbon atom are given in Table 4.

Independent of the theoretical model, the positive charge is overwhelmingly accommodated at the phenyl fragment rather than at the methylene group. As is to be expected, the 5-aminothienyl is the strongest donor group and phenyl the weakest. The π-charge of the exocyclic 'carbenium carbon' decreases in the order **8** >**9** >**10** to

only 0.18e. This is half the value expected from the Spiesecke–Schneider relationship. The total charges calculated by Mulliken population analysis (MPA) suggest an even lower decrease and aminophenyl appears as a stronger donor than aminothienyl in this theoretical model. The net atomic charges calculated by the more elaborated natural population analysis (NPA), however, reflects the results of the analysis by π-charges fairly well. This concerns both the magnitude of the intramolecular electron transfer and the above-mentioned order of the positive charge at the exocyclic carbons. However, the charge is only a qualitative measure for chemical shifts.

8   **9**   **10**
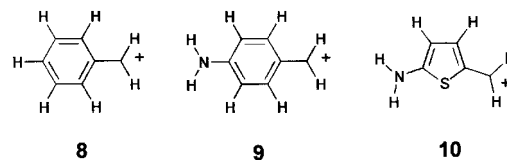
The plots of the experimental vs theoretical shifts are shown in Figure 3. The individual combinations **A–H** of the plot are defined in Table 3. The experimental and theoretical values of triphenylmethinium (plot **A**), tris(4-aminophenyl)methinium (plot **C**), tris(5-morpholino-2-thienyl)methinium (plot **G**) and tris(2-amino-5-thiazolyl)methinium ions (plot **H**) show close linear correlations. The correlation coefficients are about 0.99 or larger. According to the data in Table 3, the correlation does not deteriorate much if the morpholino group of **3b** is modelled by NMe$_2$ (**G** vs **E**).

The calculated shifts of tris(2-thienyl)methinium (**2**) are clearly at variance with the experiment. The correlation coefficient decreases to 0.91 (see Table 3, **D**). Change of the solvent did not alter the result. In the consequence, the correlation including all data of Table 3 is poor (r = 97). The chemical shifts of the carbon of the thienyl groups of **2** are shifted to higher fields than expected from theory. Abarca *et al.*[23] reported a erratic behaviour of the chemical shifts of **2** on comparing the shifts in the series tris(2-thienyl)methinium (**2**), bis(2-thienyl)phenylmethinium (**6**) and 2-thienyl(diphenyl)-methinium (**7**) in sulphuric acid relative to those of the corresponding carbinols in chloroform. If the experi-
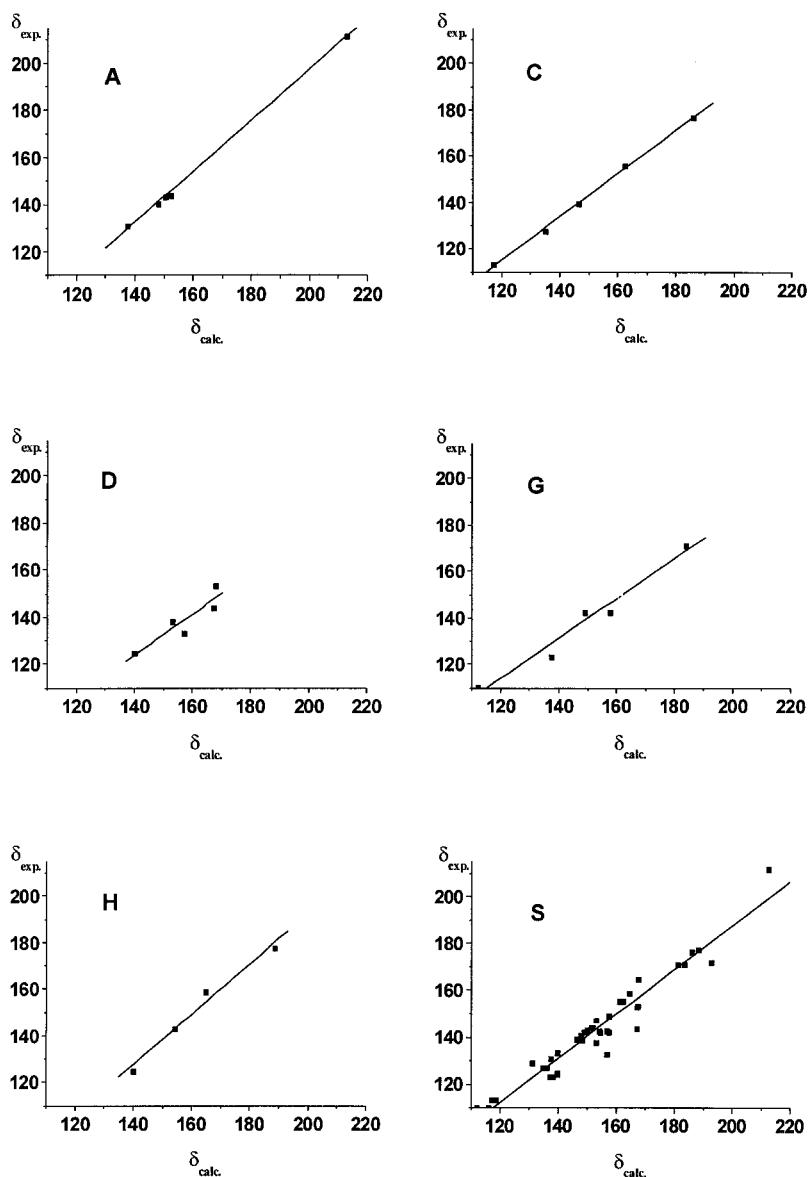
Figure 3. Plot of experimental vs theoretical chemical shifts in ppm calculated by GIAO-DFT. The capital letters **A**–**H** are defined in Table 3. The plot **S** refers to the overall correlation of all data listed in Table 3

mental shifts of **2**, **6** and **7** are calculated by DFT-GIAO the exceptional behaviour of **2** is confirmed. Whereas the mean absolute deviation of **6** and **7** amounts only to 4 ppm, the error of **2** increases to 10 ppm. Attempts failed to explain this discrepancy by structural modification of **2**. The effect of a change of the S⋯S distance of the SS-*cis* conformer **2B** or a change of the angle of twist of the thienyl rings of the propeller-shaped structure **2A** did not result in a sufficiently large decrease of the chemical shifts of **2**. In an extreme structural modification, thienyl rings are forced into a common plane. Abarca *et al.*[23] assumed the formation of the planar structure to explain the discrepancy. However, as mentioned above, planar-ization of **2** is energetically not favoured. In addition, the calculated change in chemical shifts is weak. Dimeriza-

tion of **2** in a hypothetical collinear stack also has a minor effect on the chemical shifts.

UV–VIS spectral data

The results of the calculations on the planar bis(2-thienyl)methinium (**1B**) and the propeller-shaped tris(2-thienyl)methinium **2A** and tris(5-morpholino-2-thienyl)-methinium (**4bA**) ions are listed in Table 5.

If **2A** and **4bA** display D_3 symmetry, two degenerate transitions of symmetry $E \longrightarrow A_1$ are calculated. The first two transitions bring about the longest wavelengths absorption bands in the visible and the second two the absorption band in the UV region. These lowest energy

Table 5. Calculated and spectral absorptions of **1**, **2** and **4b** in nm (calculated oscillator strengths *f* in parentheses)

| Compound | λ_{calc} (f) | | | λ_{max} (lgε) Exp.[d] |
	TD-DFT[a,e]	ZINDO/S[b,e]	PPP[c]	
1	419 (0,17)	479 (1.01)	447 (1.73)	487 (4.33)
	357 (0,52)	302 (0.28)	376 (0.20)	~375 (~4.3)
2	414 (0.24)	465 (0.61)	457 (0.73)	472 (4.55)
	414 (0.24)	465 (0.61)	457 (0.73)	
	357 (0.11)	297 (0.04)	385 (0.06)	367 (3.69)
	357 (0.11)	297 (0.04)	385 (0.06)	
4b	520 (0.56)	563 (0.75)	598 (0.70)	616 (4.97)
	520 (0.56)	563 (0.75)	598 (0.70)	
	331 (0.03)	320 (0.08)	356 (0.01)	334 (4.26)
	331 (0.03)	320 (0.08)	356 (0.01)	

[a] 6–31G(d) basis set augmented by a set of diffuse functions (cf. Ref. 15).
[b] Full configuration interaction of singly excited configurations.
[c] Full interaction of $\pi\pi^*$ singly excited configurations. For parameters see Ref. 28. The resonance integrals of the bonds to central carbon were reduced by the cosine of the torsional angle; morpholino replaced by dimethylamino substituents.
[d] **1** in sulphuric acid, **2** in methylene chloride–CF$_3$COOH and **4b** in methylene chloride.[1]
[e] There is an additional weak non-degenerate electronic transition in the UV region between the degenerate transitions.

transitions are essentially of the $\pi \rightarrow \pi^*$ type. As expected from the former calculation on polymethine dyes,[24] TD-DFRT transition energies are overestimated. The error is between 0.37 and 0.41 eV for the colour band and hence nearly twice as large as for neutral sulfur-containing compounds.[15] In the wavelength scale the error appears larger. The origin of the error is not understood. Based on the DFT optimum geometries calculations were also performed by the semiempirical ZINDO/S[14] and by the PPP (Pariser–Parr–Pople) methods[27] using, in the latter case, the formerly derived parameters.[28] The data are given in Table 5. A full singly-excited configuration interaction was employed in the all-valence electron and π-electron approximation, respectively. The absorption wavelengths of the colour bands calculated by ZINDO/S are in better agreement with the experiment than those of TD-DFRT (average errors of 0.09–0.38 eV, respectively). With an extremely low computational expenditure, the traditional PPP π-approximation[27] also works satisfactorily. In this approach, the non-planarity is taken into account by DFT geometry and by resonance integrals reduced with regard to the twisting of the molecular fragments. However, the occurrence of a very intense colour band and less intense shorter wavelength absorption band in the UV region is correctly predicted by all three methods. These transitions are essentially $\pi \rightarrow \pi^*$ in nature with dominant HOMO–LUMO contributions. On passing from **2** to **4b**, the bathochromic shift of the morpholino group is well predicted by TD-DFRT (about 0.06 eV) and by ZINDO/S (0.05 eV). Because of the unfavourable scaling of TD-DFRT with the dimension of the system, the computer time for the morpholino-substituted compound (34 'heavy atoms') is very long, but is short with semiempirical calculations. Therefore, as long as only $\pi \rightarrow \pi^*$ transitions of chromophoric compounds are of interest, the semiempirical methods perform better and are more efficient.

CONCLUSIONS

DFT calculations on Crystal Violet and triheteroaryl-methinium chromophores with three equal substituents in corresponding positions predict a propeller-shaped molecule of D_3 symmetry with dihedral angles between the plane of the substituents and the central C^+C_3 fragment of about 30°. In the case of tris(2-thienyl)methinium and derivatives, a second minimum structure was found at slightly lower energy than the symmetrical conformers. This structure has two oppositely inclined thienyl rings with the sulfur atoms posed to one another 3.35 Å in distance. The barriers to isomerization are less than 10 kcal mol^{-1}. Hence the conformers should thermally equilibrate at ambient temperatures and the chemical shifts of the conformer are averaged on the NMR time-scale. The calculated DFT GIAO ^{13}C chemical shifts of the conformers are closely similar. This enabled the experimental shifts to be tentatively assigned to the nuclei. The theoretical and experimental shift values exhibit a close correlation. In spite of the relatively large size of the molecules, heteroarylmethinium dyes can be calculated, in principle, by time-dependent density functional response theory. The results agree reasonably well with the experimental results. However, as long as the interest is directed to the colour-determining low-energy $\pi \rightarrow \pi^*$-type transitions, semiempirical approximations may more quickly lead to the same conclusion.

Supporting information

Molecular structures of the calculated cations 1–7, including transition structures, and *x*, *y*, *z* coordinates in ångstroms are available at the epoc website at http://www.wiley.com/epoc.

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