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The Tris(2-thienyl)methyl Cation Problem. A Nuclear Magnetic Resonance Spectroscopic Study†

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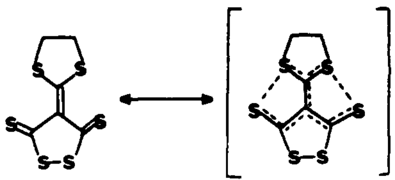
A series of homologues of the trityl cation obtained by total or partial substitution of the phenyl rings for 2- or 3-thienyl groups has been studied by ^1H and ^{13}C NMR. In general, the spectral parameters found follow the expected trends. However, a most unexpected effect is found in the transformation of tris(2-thienyl)carbinol (1d) into tris(2-thienyl)methyl cation (2d), since the increase of the total chemical shift ($\Delta\sum\delta$) associated with the ionization is as low as 105 ppm. To account for this observation, several hypotheses are discussed including the possibility of through-space charge delocalization by the three sulfur atoms and the interaction of the thiophene rings in an alternate conformation.

Introduction

Many papers have been devoted in the past to the correlation between charge density and ^1H and ^{13}C NMR chemical shift values in a variety of stable aryl-stabilized carbenium ions.[1] In contrast, studies on analogous heterocyclic systems are scarce and have shown in the case of thienyl-stabilized ions a dependence of the ^{13}C NMR response with the relative position of the carbon atoms and the heteroatom, especially for those adjacent to the sulfur atom.[2]

Recently we became interested in the correlation of NMR parameters with the ability of thienyl groups, as compared to aryl groups, to stabilize a positive charge. In the course of this study[3] the ^{13}C NMR spectra of a series of 2-thienylcarbenium ions **2** revealed an unexpected chemical shift response to the substitution of aryl by thienyl groups, and an amazing increase of the total chemical shift value, as low as 105 ppm in the transformation of the carbinol **1d** into the cation **2d**, which was tentatively identified by us as a trishomoheteroaromatic species. On the other hand, Wudl and co-workers[4] have found unexpected C–C, C–S, and S–S bond lengths in the novel sulfocarbon **3**, which was found to be a heteroaromatic trimethylenemethane embedded in a "pseudo-1,2-dithiolo-1,2-dithiole" $(4n + 2)$ π-electron milieu. In this paper we report our detailed ^1H and ^{13}C NMR study of a series of carbenium ions stabilized by thienyl groups with different types of substitution patterns in the search for a definitive explanation of the intriguing behavior of the parent ion **2d**.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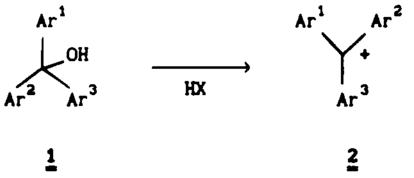
Results and Discussion

Scheme I[a]



	Ar¹	Ar²	Ar³
a	Ph	Ph	Ph
b	Ph	Ph	2-Th
c	Ph	2-Th	2-Th
d	2-Th	2-Th	2-Th
e	Ph	Ph	3-Th
f	Ph	3-Th	3-Th
g	3-Th	3-Th	3-Th
h	2-Th	2-Th	3-Me-2-Th
i	3-Me-2-Th	3-Me-2-Th	3-Me-2-Th
j	2-Th	2-Th	5-Me-2-Th
k	5-Me-2-Th	5-Me-2-Th	5-Me-2-Th
l	2-Th	2-Th	2-Fu

[a] Th = thienyl, Me = methyl, Fu = furyl.

Two series of thienyl-substituted methylcarbenium ions containing the heterocyclic ring attached to C-2 or C-3, respectively, as well as phenyl groups, were prepared upon protonation of the carbinols **1** (see Scheme I). Protonations were carried out by dissolving the corrresponding carbinol in either concentrated sulfuric acid or trifluoroacetic acid at room temperature except where otherwise specified. ^1H and ^{13}C NMR spectral data for carbinols **1** and ions **2** are given in Tables I–VI. Assignments were made by the usual methods, including gated decoupled

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† This paper is dedicated to the memory of Prof. Francisco Gaviña.

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Table I. ^{13}C NMR Chemical Shifts ($CDCl_3$)[a] of Carbinols 1

	phenyl				2 or 3-thienyl[b]				3- or 5-methyl-2-thienyl					2-furyl[b]				
no.	C_{ipso}	C_o	C_p	C_m	C_5	C_4	C_3	C_2	C_5	C_4	C_3	C_2	CH_3	C_5	C_4	C_3	C_2	C–OH
1a[c]	146.6	127.9	127.2	128.0														77.2
1b	146.5	127.8	127.4	127.2	125.4	126.7	126.3	152.2										79.9
1c	146.1	127.9	126.5	126.5	125.7	126.6	126.4	151.9										78.9
1d					125.7	126.4	126.1	151.1										76.2
1e	146.5	127.9	127.9	127.3	125.7	127.3	148.4	123.5										79.8
1f	146.1	128.0	127.4	126.8	125.8	127.6	148.3	122.9										77.8
1g					125.7	127.1	147.9	122.3										75.7
1h					126.6	126.3	126.1	150.7	122.9	131.8	135.1	143.8	15.2					75.7
1i									123.4	131.8	135.2	143.5	15.2					75.7
1j					125.7	126.2	126.6	151.6	140.4	124.7	126.2	148.8	15.4					76.1
1k									139.9	124.3	125.7	148.1	15.1					75.7
1l					125.8	126.5	126.1	149.0						142.7	110.3	108.4	156.8	74.2

[a] Internal reference $CHCl_3$ (77.2 ppm) or $CDCl_3$ (77.0 ppm). [b] Assignments were made on the basis of those for 2-methyl derivatives: Levy, G. C.; Nelson, G. L. In *13-C Nuclear Magnetic Resonance*; J. Wiley and Sons: New York, 1972. Values with range ±0.4 are interchangeable. [c] Values previously reported: 149.2, 127.7, 127.7, 127.7, 79.4. Ray, G. J.; Kurland, R. J.; Colter, A. K. *Tetrahedron* 1971, *27*, 735.

Table II. ^{13}C NMR Chemical Shifts (98% H_2SO_4)[a] of Carbenium Ions 2

	phenyl				2 or 3-thienyl				3- or 5-methyl-2-thienyl					2-furyl				
no.	C_{ipso}	C_o	C_p	C_m	C_5	C_4	C_3	C_2	C_5	C_4	C_3	C_2	CH_3	C_5	C_4	C_3	C_2	C^+
2a[b]	140.6	143.3	144.1	131.1														211.6
2b	140.9	140.0	140.0	131.3	168.9	138.0	154.6	148.2										191.5
2c	139.4	138.1	139.0	130.8	159.7	136.2	151.4	145.6										176.8
2d					143.7	124.3	137.9	132.7										153.3
2e	140.5	141.4	142.5	131.4	136.3	132.8	146.2	162.9										196.2
2f	140.0	140.0	141.1	131.1	135.2	132.2	145.0	157.8										183.6
2g					134.5	131.9	144.1	154.4										172.2
2h[c]					155.6	135.7	149.1	144.5	150.1	139.0	159.1	139.2	19.3					165.2
2i									150.7	137.8	158.4	140.2	16.1					166.3
2j[c]					149.8	132.6	145.6	141.4	161.0	134.5	149.0	141.0	17.2					176.3
2k[c]									158.7	134.1	147.8	141.0	17.9					171.2
2l[d]					151.9	133.2	146.9	139.2						161.9	120.0	141.4	152.4	153.3

[a] Internal refererence capillary dioxane (68.1 ppm). [b] Values previously reported: 139.0, 143.3, 143.1, 130.3, 210.9 ppm. Ray, G. H.; Kurland, R. J.; Colter, A. K. *Tetrahedron* 1971, *27*, 735. [c] Generated in trifluoroacetic acid. [d] Generated in trifluoromethanesulfonic acid.

Table III. Differences ($\Delta\sum\delta$ in ppm) between $\sum\delta$ for the Ions and Carbinols[a]

1 → 2	$\Delta\sum\delta$	$\Delta_{Ph}\sum\delta$	$\Delta_{Th_1}\sum\delta$	$\Delta_{Th_2}\sum\delta$	$\Delta_{Th_3}\sum\delta$	$\Delta_{Th_4}\sum\delta$	$\Delta_{Fu}\sum\delta$
1a → **2a**	278.1	47.9					
1b → **2b**	269.9	39.6	79.1				
1c → **2c**	257.3	34.8	62.3				
1d → **2d**	105.0		9.3				
1e → **2e**	257.3	43.8		53.3			
1f → **2f**	237.4	40.4		45.6			
1g → **2g**	222.2			41.9			
1h → **2h**	257.8		55.2		57.9		
1i → **2i**	252.9				54.1		
1j → **2j**	226.0		39.3			47.2	
1k → **2k**	232.3					45.6	
1l → **2l**	224.2		43.8				57.5

[a] Th_1 = 2-thienyl; Th_2 = 3-thienyl; Th_3 = 3-methyl-2-thienyl; Th_4 = 5-methyl-2-thienyl; Fu = 2-furyl.

Table IV. Differences ($\Delta\delta$ in ppm) between Corresponding Ring Positions of Ions and Related Carbinols

	phenyl				2 or 3-thienyl				3- or 5-methyl-2-thienyl					2-furyl				
1 → 2	C_{ipso}	C_o	C_p	C_m	C_5	C_4	C_3	C_2	C_5	C_4	C_3	C_2	CH_3	C_5	C_4	C_3	C_2	C^+
1a → **2a**	−6.0	15.4	16.9	3.1														134.4
1b → **2b**	−5.6	12.2	12.6	4.1	43.5	11.3	28.3	−4.0										111.6
1c → **2c**	−6.7	10.2	12.5	4.3	34.0	9.6	25.0	−6.3										97.9
1d → **2d**					18.0	−2.1	11.8	−18.4										77.1
1e → **2e**	−6.0	13.5	14.6	4.1	10.6	5.5	−2.2	39.4										116.4
1f → **2f**	−6.1	12.0	13.7	4.4	9.4	4.6	−3.3	34.9										105.8
1g → **2g**					8.8	4.8	−3.8	32.1										96.5
1h → **2h**					29.0	9.4	23.0	−6.2	27.2	7.2	24.0	−4.6	4.1					89.5
1i → **2i**									27.3	6.0	23.2	−3.3	0.9					90.6
1j → **2j**					24.1	6.4	19.0	−10.2	20.6	9.8	22.8	−7.8	1.8					100.2
1k → **2k**									18.8	9.8	22.1	−7.1	2.8					95.5
1l → **2l**					26.1	6.7	20.8	−9.8						19.2	9.7	33.0	−4.4	79.1

spectra, considerations of relative signal intensities, and molecular symmetry. The following parameters were used for the study of the series: the difference ($\Delta\sum\delta$) of the total chemical shift value ($\sum\delta$) for the ions and the parent carbinols, the difference ($\Delta_{Ph}\sum\delta$ or $\Delta_{Th}\sum\delta$) of the total chemical shift value in each ring associated with the ionization (Table III), and the chemical shift difference ($\Delta\delta$) for corresponding ring positions (Table IV).

Table V. ^{1}H NMR Chemical Shifts[a] for Carbinols 1[b]

no.	chemical shift
1a	7.3 (m, 15 H), 2.6 (br s, 1 OH)
1b	7.3–6.9 (m, 11 H), 6.7–6.5 (m, 2 H), 2.8 (br s, 1 OH)
1c	7.2–6.9 (m, 7 H), 6.8 (m, 4 H), 3.0 (br s, 1 OH)
1d	7.5–7.4 (m, 3 H), 7.3–7.1 (m, 6 H), 3.0 (br s, 1 OH)
1e	7.3–7.0 (m, 11 H), 6.9–6.7 (m, 2 H), 2.9 (br s, 1 OH)
1f	7.4–7.2 (m, 7 H), 7.2–6.9 (m, 4 H), 2.8 (br s, 1 OH)
1g	7.1–7.0 (m, 3 H), 6.9–6.7 (m, 6 H), 2.7 (br s, 1 OH)
1h	7.2–6.9 (m, 2 H), 6.8 (d, J = 5 Hz, 1 $H_{5'}$), 6.7–6.5 (m, 4 H), 6.5 (d, J = 5 Hz, 1 $H_{4'}$), 3.1 (br s, 1 OH), 1.8 (s, 3 H)
1i	6.9 (d, J = 5 Hz, 3 H_5), 6.6 (d, J = 5 Hz, 3 H_4), 2.9 (br s, 1 OH), 2.0 (s, 9 H)
1j	7.0 (dd, J = 5 Hz, J = 1 Hz, 2 H_5), 6.8 (m, 4 H), 6.7–6.3 (m, 2 H), 3.4 (br s, 1 OH), 2.3 (s, 3 H)
1k	6.6 (d, J = 4 Hz, 3 H), 6.4 (d, J = 4 Hz, 3 H), 3.1 (br s, 1 OH), 2.4 (s, 9 H)
1l	7.2–6.8 (m, 3 H), 6.8–6.5 (m, 4 H), 6.2–5.8 (m, 2 H), 3.7 (br s, 1 OH)

[a] δ ppm, TMS. [b] Positions other than those of the parent 2-thienyl rings are denoted *n*′.

Table VI. ^{1}H NMR Chemical Shifts for Carbenium Ions 2[a] in H_2SO_4 Solution

no.	chemical shift
2a	8.1–7.4 (m, 15 H)
2b	9.5 (d, J = 5 Hz, 1 H_5), 8.2 (d, J = 4 Hz, 1 H_3), 7.9 (dd, J = 5 Hz, J = 4 Hz, 1 H_4), 7.7–7.4 (m, 10 H)
2c	8.9 (d, J = 5 Hz, 2 H_5), 8.0 (d, J = 4 Hz, 2 H_3), 7.7–7.5 (m, 5 H), 7.6 (dd, J = 5 Hz, J = 4 Hz, 2 H_4)
2d	8.9 (d, J = 5 Hz, 3 H_5), 7.8 (d, J = 4 Hz, 3 H_3), 7.4 (dd, J = 5 Hz, J = 4 Hz, 3 H_4)
2e	8.7 (dd, J = 2 Hz, J = 1 Hz, 1 H_2), 7.3–8.0 (m, 12 H)
2f	8.5 (dd, J = 2 Hz, J = 1 Hz, 2 H_2), 8.2–7.3 (m, 9 H)
2g	8.2 (dd, J = 2 Hz, J = 1 Hz, 3 H_2), 7.5 (dd, J = 5 Hz, J = 2 Hz, 3 H_5), 7.2 (d, J = 5 Hz, 3 H_4)
2h	8.6 (d, J = 5 Hz, 2 H_5), 8.4 (d, J = 5 Hz, 1 $H_{5'}$), 7.9 (d, J = 4 Hz, 2 H_3), 7.6 (dd, J = 5 Hz, J = 4 Hz, 2 H_4), 7.4 (d, J = 5 Hz, 1 $H_{4'}$), 2.1 (s, 3 H)
2i	8.1 (d, J = 5 Hz, 3 H_5), 7.0 (d, J = 5 Hz, 3 H_4), 1.9 (s, 9 H)
2j	8.4 (d, J = 5 Hz, 2 H_5), 7.8 (d, J = 5 Hz, 3 $H_{3,3'}$), 7.4 (dd, J = 5 Hz, J = 4 Hz, 3 $H_{4,4'}$), 2.7 (s, 3 H)
2k	7.5 (d, J = 4 Hz, 3 H_3), 7.0 (d, J = 4 Hz, 3 H_4), 2.4 (s, 9 H)
2l	8.4 (d, J = 5 Hz, 2 H_5), 8.2 (d, J = 1 Hz, 1 $H_{5'}$), 7.9 (d, J = 4 Hz, 2 H_3), 7.8 (d, J = 3 Hz, 1 $H_{3'}$), 7.4 (dd, J = 5 Hz, J = 4 Hz, 2 H_4), 6.6 (d, J = 3 Hz, 1 $H_{4'}$)

[a] Positions other than those of the parent 2-thienyl rings are denoted *n*′.

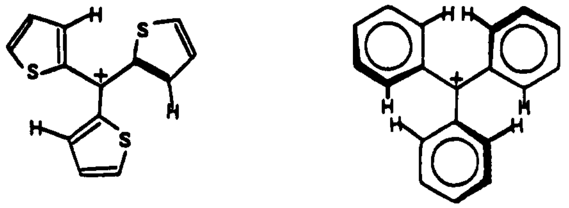

Figure 1. Coplanar alternate conformation in cation **2d** free of steric hindrance and H–H interannular interaction in trityl cation.

The different effectiveness of the thienyl ring to delocalize the positive charge depending on the attachment position is clearly shown by the trend observed in the $\Delta_{\mathrm{Ph}}\sum\delta$ (see Table III) value for the remaining phenyl groups in the conversion **1** → **2**. The thienyl ring, when attached to the carbenium center by C-2, was found to be more effective in the delocalization of the positive charge as reflected by the lower increase of the $\Delta_{\mathrm{Ph}}\sum\delta$ value for the phenyl rings in the conversion **1b** → **2b** (39.6 ppm) if related to **1e** → **2e** (43.8 ppm). It is to be noted that there is no correlation between the increase of the total chemical shift value $\Delta\sum\delta$ and the ability of the heterocyclic ring to delocalize the charge. For instance, the $\Delta\sum\delta$ value for the transformation **1b** → **2b** is 269.9 ppm, while for the transformation **1e** → **2e**, which involves the less effective 3-thienyl group, $\Delta\sum\delta$ is 257.3 ppm. On the other hand, the increase of $\Delta_{\mathrm{Th}}\sum\delta$ for the 2-thienyl ring (79.1 ppm) in the ionization of **1b** is greater than the observed value in the case of **1e** (53.3 ppm). All these observations suggest that the sulfur atom localizes more positive charge when the thiophene ring is attached to the carbenium center at C-3. This is consistent with the greater length of the chromophore in the 2-thienyl ring. The shielding of the central carbon in ions **2a**, **2b**, and **2e** appears to increase with the ability of the substituents to delocalize positive charge, as expected (see Table II). Substitution of a second phenyl ring in ion **2a** by a 2-thienyl or 3-thienyl group (ions **2c** and **2f**) results in the progressive shielding of the central carbon and decreased values for $\Delta_{\mathrm{Ph}}\sum\delta$, in the remaining phenyl ring, although in these cases the effect of the substitution is less noticeable as expected by the application of the principle of increasing of the electron demand.[5] These observations are in good agreement with the results obtained by Tiecco and co-workers[2b] in the ^{1}H NMR study of a series of *p*-tolylthienyl carbenium ions.

However, when the phenyl group in ions **2c** and **2f** was substituted by a 2-thienyl or 3-thienyl group, respectively (ions **2d** and **2g**), a different type of response in the NMR parameters was observed in each case. So, all the spectral parameters of ion **2g** follow the expected trends in the series **2b**, **2c**, **2e**, and **2f**, the $\Delta\sum\delta$ value for the ionization of **1g** being 222.2 ppm. By contrast, in the case of ion **2d** there is a most unexpected effect on the $\Delta\sum\delta$ parameter, which reaches a value as low as 105 ppm, which can almost be accounted for in terms of rehybridization of the central carbon atom. If the normal increase of $\Delta\sum\delta$ (over 200 ppm, see Table III) for this type of transformation[6] has to be related to localization of positive charge on the carbon(s), it appears that very little charge, if any, is present on the ring carbons of the thienyl groups in the cation **2d** and, hence, that the charge is almost exclusively localized on the three sulfur atoms. At first, this should imply little or no deshielding of the ring protons in ^{1}H NMR by the transformation **1d** → **2d** as these protons would not be bonded to positively charged carbons. However, the deshielding of the thienyl protons in ion **2d** follows the trend shown in ions **2b** and **2c** (see Table VI).

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(5) Brown, H. C.; Schleyer, P. v. R. *The Non Classical Ion Problem*; Plenum: New York, 1977; p 163.

(6) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

To explain the above results, some especial structural feature must be assumed for the tris(2-thienyl)carbenium ion (**2d**).

An examination of molecular models shows that ion **2d** might adopt a coplanar alternate conformation free of steric hindrance due to the absence of interannular H–H interactions (Figure 1). In this conformation, the charge could be delocalized very effectively through the three equivalent thienyl groups since in VB terms all the canonical structures are equivalent and can contribute to the resonance hybrid without the necessity of any conformational change. By contrast, this is not the case for ions **2a–c** and **2e–g** where the three rings cannot remain simultaneously in the same plane.

To confirm the validity of our hypothesis of the existence of a stable planar conformation that accounts for the disturbance found on the spectral parameters, we synthesized the carbinols **1h** and **1i** as precursors upon protonation of the ions **2h** and **2i** in which one or more of the thienyl rings must be forced out of the plane by the steric hindrance introduced by the methyl groups attached at C-3 in the 2-thienyl ring. The stability of carbinols **1h** and **1i** was lower than that of the remaining members in the series, and they showed a remarkable tendency to polymerize. While all the nonsubstituted cations could be prepared by protonation of the carbinols in concentrated sulfuric acid and their spectra registered at room temperature, ion **2h** had to be studied below 5 °C. The observed value for the $\Delta\sum\delta$ parameter for the transformation **1h** → **2h** was 257.8 ppm, which is very close to that associated with the transformation **1c** → **2c** (257.3 ppm). Consequently, charge delocalization in ion **2h** appears to follow the same scheme as in the phenyl-group-containing cations studied above. On the other hand, the increment of the total chemical shift value for the unsubstituted thiophene ring ($\Delta_{Th}\sum\delta$ = 55.2 ppm) in **2h** is smaller than the increment for the 3-methyl-substituted ring (57.9 ppm). This is the expected behavior for ion **2h** since the more substituted an aromatic ring is, the greater increase of the total chemical shift value is usually found in the ionization.

Complete substitution of hydrogen by methyl groups on C-3 in the remaining thiophene rings leads to cation **2i**. This ion could not be observed in sulfuric acid solution due to polymerization, but was prepared and studied by protonation of **1i** in trifluoroacetic acid at room temperature. The $\Delta\sum\delta$ value found in the transformation **1i** → **2i** was in this case 252.9 ppm, a value very similar to that found in the ionization of **1h**. Then, it can be concluded that the structural perturbation introduced by a single methyl group is enough to cancel all the special spectroscopical features shown by ion **2d**.

The above observations support the hypothesis on the relationship between the anomalous spectral behavior shown by ion **2d** and its ability to adopt a stable planar conformation. However, between ion **2d** and ions **2h** and **2i** there exist also differences from the electronic point of view since the charge delocalization pattern has been affected by alkyl substitution.[7] For this reason we have synthesized two new cations, **2j** and **2k**, in which the charge distribution is perturbed by methyl substitution at position C-5 without introducing any steric hindrance to the potential coplanarity. Surprisingly, the ^{13}C NMR behavior of these cations does not resemble that of ion **2d**. The values of $\Delta\sum\delta$ for the transformations **1j** → **2j** and **1k** → **2k** were 226.0 and 232.3 ppm, respectively. The increment of the total chemical shift value in the ionization **1j** → **2j** was greater in the 5-methyl-substituted thiophene ring following the same trend as in the 3-methyl-substituted ring of ion **2h**. All the above facts show that tris(2-thienyl)carbenium ion (**2d**) exhibits a singular spectroscopic behavior that must involve the existence of some particular charge delocalization pattern which is inhibited even by small stereoelectronic modifications such as single methyl substitution.

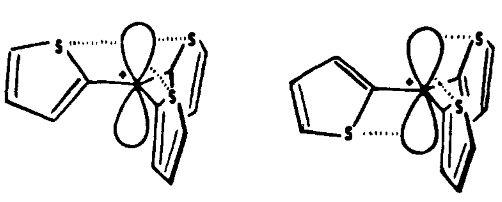

Figure 2. Direct delocalization of the positive charge through space by sulfur atoms in cation **2d**.

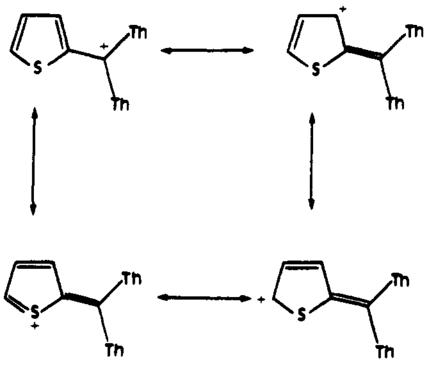

Figure 3. Schematic representation of charge delocalization by π conjugation in the title ion **2d**.

To determine whether the presence of sulfur in the heterocyclic moiety is determinant to give rise to the unusual low value of $\Delta\sum\delta$ associated with the ionization of **1d**, we prepared the alcohol **1l** containing two 2-thienyl groups and one 2-furyl group. The protonation of **1l** in sulfuric acid at room temperature gave polymeric materials. However, the ion **2l** could be observed in trifluoromethanesulfonic acid when the protonation was carried out at −10 °C. In this case the value of $\Delta\sum\delta$ associated with the transformation **1l** → **2l** was 224.2 ppm. On the other hand, the charge is localized now in the 2-furyl group ($\Delta_{Fu}\sum\delta$ = 57.5 ppm) to a greater extent than in the thiophene rings ($\Delta_{Th}\sum\delta$ = 43.8 ppm). This is in good agreement with previous literature data.[2f] From these experiments we can conclude the direct involvement of the especial nature of the sulfur atoms and the requirement of the presence of three unsubstituted thiophene rings as sources of the anomalous shielding of the carbon atoms observed in **2d**.

To account for these observations, at first, several explanations can be suggested: (a) The sulfur localizes most of the charge in ion **2d**, (i) interacting directly with the empty p orbital at the central carbon through space[8] (Figure 2) or (ii) by usual π conjugation (Figure 3). (b) A peripheral ring current involving 14 π electrons is established through space, having three interruptions in the σ framework, resembling a trishomoheteroaromatic system[9] with, uniquely, the discontinuities in the π system resulting from lack of σ bonding rather than from the insertion of methylene groups (Figure 4). This current would shield very particularly the central carbon.

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[7] 5-Ethyl-2-furyl is a better substituent than the 2-furyl group to delocalize a positive charge (see ref 2f).

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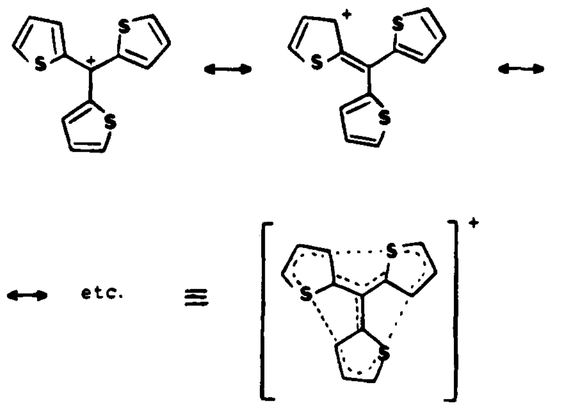

Figure 4. Schematic representation of the title ion describing the potential 14-π-electron peripheral trishomoheteroaromatic-like ring current.

Several arguments can be found in support of and against the suggested hypotheses:

(a) (i) It should be possible for the interaction through space of the sulfur atoms with the cationic center to be exerted successively by one, two, or three sulfur atoms in an additive manner, the only condition being that the empty p orbital of the central carbon and the *interacting* sulfur in the thiophene ring(s) have the correct orientation. Then, there is no apparent requirement for the three thiophene rings to interact *simultaneously* as found. On the other hand, methyl substitution especially at C-5 should not be expected to disturb this type of charge delocalization.

(a) (ii) Recent studies by Nakayama et al. on the reactivity of **2d** with hydrogen and carbon nucleophiles[10] denote positions C-3, C-5, and the central carbon as supporting most of the positive charge density. This would suggest π-charge delocalization. However, little if any charge localization at these positions is suggested by the chemical shift values of these carbon atoms in ^{13}C NMR. Moreover, this type of charge delocalization pattern should be reinforced by substitution of thiophene by furan since this latter ring is a better π donor by conjugation[2f] involving finally a canonical structure of oxonium ion. 5-Methyl-substituted thiophene rings in ions **2j** and **2k** do not introduce steric hindrance to conformational changes, and they are also better π donors than the parent 2-thienyl group.

(b) The existence of a homoaromatic-like ring current in **2d** justifies that the effect of the thienyl rings on the spectral parameters is not additive and also that it is suppressed when a furyl group is introduced for thiophene. On the other hand, a delocalized 14-π-electron system is expected to induce a noticeable ring-current effect for the protons. From the ^1H NMR data there is no indication of such an effect.

Conclusions

Cation **2d** shows a unique charge-delocalization pattern in the series of tri(hetero)arylcarbenium ions which is reflected in the low value of the $\Delta\sum\delta$ parameter associated with the ionization **1d** → **2d**. None of the hypotheses suggested to account for this effect can be disregarded by the fact that it is canceled by methyl substitution at the C-5 thiophene position. It only means that methyl-substituted ions **2j** and **2k** reach an energy minimum by classical charge π delocalization in a conjugate polyene with a terminal tertiary carbon. Although proof (or disproof) of the operation of a novel 14-π-type aromaticity or the simultaneous direct through-space interaction of three sulfur atoms with a carbenium center in a freely rotating framework is an interesting challenge, to the best of our knowledge no further information can be obtained by application of ^1H and ^{13}C NMR techniques to the tris(2-thienyl)methyl cation (**2d**) problem. Work is in progress to determine the solid-state structure of this intriguing ion.

Experimental Section

Melting points were determined on a Reichert melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 843 instrument. The NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B or a Bruker WP-80-SY or AM-200 spectrometer, both equipped with a low-temperature probe. The chemical shifts (ppm) were determined for neutral species relative to TMS as internal standard in Cl_3CD solution. In the case of cations, the chemical shifts (ppm) were determined relative to external (capillary) dioxane.

Preparation of 2-Thienylcarbinols. General Procedure. To a solution of the corresponding carbonyl compound in dry ether was added dropwise the equivalent amount of 2-thienyllithium under an argon atmosphere. The solution was then stirred at room temperature, and subsequently it was hydrolyzed by a mixture of ammonium hydroxide and ammonium chloride. The reaction time and purification procedure are given for each compound.

Diphenyl-2-thienylcarbinol (1b). The co-reagent was benzophenone. The reaction time was 40 h. Compound **1b** was isolated by recrystallization from hexane in quantitative yield; mp 126–127 °C (lit.[11] mp 128 °C).

Phenylbis(2-thienyl)carbinol (1c). The co-reagent was methyl benzoate. The reaction time was 48 h. The ethereal extracts from the hydrolysis mixture were evaporated, and the residue separated by a silica column, eluting with chloroform, gave the carbinol **1c** (50% yield); mp 90 °C (hexane) (lit.[11] mp 90–91 °C).

Tris(2-thienyl)carbinol (1d). The co-reagent was ethyl chloroformate. The reaction time was 48 h. Compound **1d**[2a] was purified by crystallization from hexane (65% yield); mp 63–64 °C.

General Procedure for the Preparation of 3-Thienylcarbinols. To a solution of 3-thienyllithium in dry ether was added the equivalent amount of the corresponding carbonyl compound at −70 °C under an argon atmosphere. The solution was stirred for 2 h at the same temperature and then was allowed to reach room temperature and stirred for an additional 50 h. After hydrolysis with a saturated solution of ammonium chloride, the reaction mixture was extracted with ether and the organic layer dried (Na_2SO_4) and evaporated. The purification procedure is given for each compound.

Diphenyl-3-thienylcarbinol (1e). The co-reagent was benzophenone. The reaction crude was purified by crystallization from hexane (79% yield); mp 148–149 °C. Anal. Calcd for $C_{17}H_{14}OS$: C, 76.69; H, 5.26; S, 12.03. Found: C, 76.92; H, 5.69; S, 12.13.

Phenylbis(3-thienyl)carbinol (1f). Methyl benzoate was the co-reagent. Compound **1f** was purified by crystallization from hexane (66% yield); mp 135 °C. Anal. Calcd for $C_{15}H_{12}OS_2$: C, 66.18; H, 4.47; S, 23.57. Found: C, 66.44; H, 4.08; S, 23.87.

Tris(3-thienyl)carbinol (1g).[2a] The co-reagent was ethyl chloroformate. The crude was purified by crystallization from hexane (40% yield); mp 114–115 °C.

(3-Methyl-2-thienyl)bis(2-thienyl)carbinol (1h) was prepared by the general procedure described for the preparation of 2-thienylcarbinols. The co-reagent was 3-methyl-2-thienyl 2-thienyl ketone. The reaction time was 24 h. After hydrolysis the mixture was extracted with ether, filtered, and evaporated. The crude residue was purified (dichloromethane) on a silica column. Compound **1h** was obtained as an unstable yellow oil (68% yield) that decomposes *prior to elemental analysis* (*characterized by* spectroscopical methods; see Tables I and V).

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[10] Ishii, A.; Nakayama, J.; Endo, Y.; Hoshino, M. *Tetrahedron Lett.* **1990**, *31*, 2623.

[11] Ancizar-Sordo, J.; Bistrzycki, A. *Helv. Chim. Acta* **1931**, *14*, 141.

Tris(3-methyl-2-thienyl)carbinol (1i). To a solution of (3-methyl-2-thienyl)lithium (37.6 mmol) in dry ether was added an ethereal solution of ethyl chloroformate (12.5 mmol) dropwise with stirring at −70 °C under an argon atmosphere. The stirring was continued for 2 h at the same temperature, and then the solution was allowed to warm up to room temperature and the stirring continued for 24 h. After hydrolysis with a saturated solution of ammonium chloride, the reaction mixture was extracted with ether and the organic layer was dried (Na_2SO_4) and evaporated under vacuum at room temperature. Compound 1i was recrystallized from hexane (31% yield); mp 92 °C. Anal. Calcd for $C_{16}H_{16}OS_3$: C, 60.00; H, 5.00; S, 30.00. Found: C, 59.99; H, 5.23; S, 30.29.

(5-Methyl-2-thienyl)bis(2-thienyl)carbinol (1j) was prepared by the general procedure described for the preparation of 2-thienylcarbinols. The co-reagent was 2-carbethoxy-5-methylthiophene.[12] The reaction time was 24 h. The carbinol 1j was obtained as an oil (75% yield) and was characterized by spectroscopical methods.

Tris(5-methyl-2-thienyl)carbinol (1k). To a solution of (5-methyl-2-thienyl)lithium (32 mmol) in dry ether was added an ethereal solution of ethyl chloroformate (10.5 mmol) dropwise with stirring at −5 °C. The stirring was continued for 16 h at room temperature. After hydrolysis with a saturated solution of ammonium chloride, the reaction mixture was extracted with ether. The organic layer was dried (Na_2SO_4) and evaporated under vacuum at room temperature. Alcohol 1k was recrystallized from hexane (45% yield). Anal. Calcd for $C_{16}H_{16}OS_3$: C, 60.00; H, 5.00; S, 30.00. Found: C, 60.02; H, 5.13; S, 30.08.

2-Furylbis(2-thienyl)carbinol (1l) was prepared by the general procedure described for the preparation of 2-thienylcarbinols. The co-reagent in this case was ethyl 2-furoate. The reaction time was 24 h. The residue obtained showed a great tendency toward polymerization and could not be purified. The yield (95%) is based on integration of the NMR spectra.

Preparation of Carbocations. Carbinols 1 (200 mg) were added to sulfuric acid (96%, 1 mL) with vigorous stirring at room temperature except where otherwise specified, and the NMR spectra of the resulting solutions were recorded. Carbinols 1h, 1j, and 1k were previously dissolved in chloroform (1 mL), and the protonation was performed at 4 °C. Trifluoroacetic acid was used for the protonation of 1i due to the instability of ion 2i in sulfuric acid solution. Alcohol 1l was protonated at −10 °C with trifluoromethanesulfonic acid in a chloroform (1 mL) solution.

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[12] 2-Carbethoxy-5-methylthiophene was prepared in ethanol and sulfuric acid from 5-methylthiophene-2-carboxylic acid. This compound was obtained by reaction of (5-methyl-2-thienyl)lithium with CO_2 (see ref 13).

[13] Gilman, H.; St. John, N. B.; Schulze, F. *Organic Syntheses*; John Wiley & Sons: New York, 1943; Collect. Vol. II, p 425.

Transmission of Polar Substituent Effects in the Adamantane Ring System As Monitored by ^{19}F NMR: Hyperconjugation as a Stereoinductive Factor[1]

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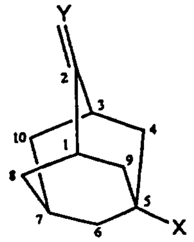
A limited series of (*E*)- and (*Z*)-5-substituted adamant-2-yl fluorides 8 and 9, respectively, has been synthesized and characterized, and the ^{19}F chemical shifts have been measured in several solvents. A wide range of ^{19}F substituent chemical shifts (SCS, ppm) are obtained for the former system (ca. 9.1 (c-C_6H_{12}), 9.6 ($CDCl_3$), and 11.8 (HFIP)) compared to the latter (ca. 0.6 (c-C_6H_{12}), 0.7 ($CDCl_3$), and 2.3 (HFIP)). Factorization of the ^{19}F SCS into polar field ($\rho_F\sigma_F$) and residual contributions (^{19}F SCS − $\rho_F\sigma_F$) reveals the predominance of the latter solvent-independent component for the *E* fluorides (8). Comparison of 8 with a similar dissection of the ^{19}F SCS of 4-substituted bicyclo[2.2.2]oct-1-yl fluorides 2 strongly suggests that the origin of the large residual contributions for 8 is "through-three-bond" electron delocalization or double hyperconjugation. The importance of this long-range electronic mechanism as a factor governing π-facial diastereoselection in 2,5-disubstituted adamantanes (1) is discussed. In particular, the assertion that the *p*-anilino substituent is an electron donor group at remote probe or reaction sites in saturated systems is addressed.

Introduction

Several recent papers by le Noble and co-workers[2] have reported on the effectiveness of 2,5-disubstituted adamantanes (1) as model systems for investigating the electronic effects of substituents on the stereoselectivity of addition reactions to trigonal carbon. These studies have disclosed several instances where a 5-substituent (X), depending on its electronic character, induces predominantly either anti or syn approach of the attacking species at the 2-position (see Chart I). This stereoselectivity has been rationalized in terms of a model proposed by Cieplak[3] that emphasizes the importance of transition-state sta-



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