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TRIS(2-THIENYL)METHYL CATION; AN UNPRECEDENT ^{13}C NMR BEHAVIOR

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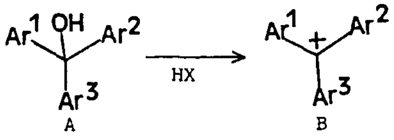
ABSTRACT: An unexpected response of the chemical shift value to the substitution of phenyl by thienyl groups is found in the series **1**-**8**. On this basis the planar cation **7** appears to show an homoaromatic-like peripheral ring current.

In contrast to the numerous reports on the formation and properties of stable aryl carbenium ions,[1] studies on thienyl carbenium ions are scarce.[2-7] Attemps to determine the ability of a thienyl group to stabilize a positive charge, as well as a comparison of the stabilizing ability of the phenyl and the thienyl rings through their ^{1}H nmr parameters have been reported.[3-6] The structure and charge distribution of some thienyl sustituted carbenium ions has also been studied by ^{13}C nmr, as this technique can be used to monitor more accurately changes in the charge distribution on cationic species.[7,8] We report here our detailed ^{13}C nmr study of a series of 2-thienyl carbenium ions **5**-**7**[9] revealing an unexpected chemical shift response to the substitution of aryl by thienyl groups, and an amazingly small increase of the total chemical shift value, 105 ppm, in the transformation of the carbinol **3** into the cation **7**.



A	B	
1	**5**	$Ar^1 = Ar^2 =$ Phenyl, $Ar^3 =$ 2-Thienyl
2	**6**	$Ar^1 =$ Phenyl, $Ar^2 = Ar^3 =$ 2-Thienyl
3	**7**	$Ar^1 = Ar^2 = Ar^3 =$ 2-Thienyl
4	**8**	$Ar^1 = Ar^2 = Ar^3 =$ Phenyl

HX= 98% H_2SO_4 or CF_3COOH

Figure 1

^{13}C Chemical shifts for carbinols **1**-**4** and ions **5**-**8** are reported in Tables 1 and 2. Assignments were made by the usual methods including the gate noise technique, considerations of relative signal intensities, and molecular symmetry. It can be observed that the progressive substitution of a phenyl by a 2-thienyl group causes a gradual shielding of the carbenium center indicating, as it has been suggested,[4-6] that the 2-thienyl is more effective than the phenyl group in stabilizing the positive charge.

Table 1.- ^{13}C nmr chemical shifts $(CDCl_3)^a$ of carbinols **1-4**

	2-thienyl[b]				phenyl				
Compound	C_5	C_4	C_3	C_2	C_{ipso}	C_o	C_p	C_m	**C-OH**
1	125.4	126.7	126.3	152.2	146.5	127.8	127.4	127.2	79.9
2	125.7	126.6	126.4	151.9	146.1	127.9	126.5	126.5	78.9
3	125.7	126.4	126.1	151.1					76.2
4[c]					146.6	127.9	127.2	128.0	77.2

a.- Internal reference $CHCl_3$(77.2 ppm) or $CDCl_3$ (77.0 ppm). b.- Assignments were made based on those for 2-methylthiophene ,G.C.Levy and G.L.Nelson in '^{13}C Nuclear Magnetic Resonance', J.Wiley and sons, N.Y. (1972). Values with range ± 0.4 ppm are interchangeable . c.- Values previously reported 149.2, 127.7, 127.7, 127.7, 79.4 ; G.J.Ray, R.J. Kurland and A.K.Colter, Tetrahedron, 27,735 (1971).

Table 2.- ^{13}C nmr chemical shifts and ^1J C-H coupling constants (98% $H_2SO_4)^a$ of carbenium ions **5-8**

	2-thienyl				phenyl				
Compound	C_5	C_4	C_3	C_2	C_{ipso}	C_o	C_p	C_m	$^+CAr^3$
5	168.9 [188]	138.0 [178]	154.6 [175]	148.2	140.9	140.0 [165]	140.0 [165]	131.3 [167]	191.5
6	159.7 [188]	136.2 [180]	151.4 [175]	145.6	139.4	138.1 [167]	139.0 [167]	130.8 [167]	176.8
7	143.7 [188]	124.3 [175]	137.9 [174]	132.8					153.3
8[b]					140.6	143.3	144.1	131.1	211.6

a.- Internal reference capilary dioxane (68.1 ppm). Coupling constants (Hz) are in brackets. b.- Values previously reported 139.0, 143.3, 143.1, 130.3, 210.9 ppm; G.H.Ray, R.J.Kurland, and A.K.Colter, Tetrahedron, 27, 735 (1971).

Table 3.- Differences ($\Delta\Sigma\delta$ in ppm) between $\Sigma\delta$ for the ions and carbinols

	5 → **1**	**6** → **2**	**7** → **3**	**8** → **4**
$\Delta\Sigma\delta$	269.9	257.6	105	278.1

Table 4.- Differences ($\Delta\delta$ in ppm) between corresponding ring positions of ions and related carbinols

	2-thienyl				phenyl				
Transformation	$\Delta\delta C_5$	$\Delta\delta\ C_4$	$\Delta\delta\ C_3$	$\Delta\delta\ C_2$	$\Delta\delta\ C_{ipso}$	$\Delta\delta C_o$	$\Delta\delta\ C_p$	$\Delta\delta\ C_m$	$\Delta\delta\ ^+CAr_3$
1 → **5**	+43.2	+11.3	+28.6	-4.0	-5.6	+12.2	+12.6	+4.1	+111.6
2 → **6**	+34.0	+9.6	+25.0	-6.3	-6.7	+10.2	+12.5	+4.3	+98.2
3 → **7**	+18.0	-2.1	+11.8	-18.4					+77.1
4 → **8**					-6.0	+15.4	+16.9	+3.1	+134.4

The following parameters were used for the study of the series: The diference ($\Delta\Sigma\delta$, Table 3) of the total chemical shift value ($\Sigma\delta$) for the ions and the parent carbinols, and the chemical shift difference ($\Delta\delta$, Table 4) for corresponding ring positions in these two types of compounds.

When one phenyl group is at least present, the effect of the substitution of phenyl by 2-thienyl groups on the $\Delta\Sigma\delta$ values (Table 3) follows the trends expected by the application of the principle of increasing of the electron demand,[10] and consequently it is not additive. However, when the last phenyl group is susbstituted by thienyl there is a most unexpected effect on this parameter, the value found being only 105 ppm, which can almost be accounted for in terms of rehybridization of the central carbon atom. If the normal increase of $\Sigma\delta$ (225 ppm or more[12]) for this type of transformation has to be related to localization of positive charge on the carbon(s), it appears to be that very little charge is present on the ring carbons of the thienyl group in cation **7**.

To explain these results some new structural feature must be assumed for the tris(2-thienyl)methyl carbenium ion **7**. An examination of molecular models shows that it can adopt a coplanar alternate conformation free of steric hindrance due to the absencee of interanular H-H interactions (Figure 2).

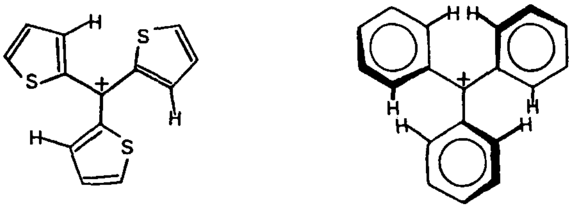


Figure 2

In this conformation, the charge could be localized very effectively at once through the three equivalent thienyl groups since in VB terms all the canonical structures are equivalent and can contribute to the resonance hybrid. By contrast, this is not the case for ions **5**, **6**, and **8** where all the rings cannot remain simultaneously planar with the delocalized cation[13]. The low value of $\Delta\Sigma\delta$ found in ion **7** would suggest that the charge is almost exclusively localized in the three sulfur atoms. This should imply little or no deshielding of the ring protons in ^{1}H nmr by the transformation **3**→**7**, as these protons are not bonded to positively charged carbons.[14] Surprisingly, the deshielding of the thienyl protons in ion **7** is similar in value to that observed in ions **5** and **6** (Table 5).

Table 5.- ^{1}H chemical shift (δ ppm, TMS) for thienyl carbenium ions 5-7 in TFA solution

Compound	2-thienyl			phenyl
	δH_5	δH_4	δH_3	
5	9.5 (d)	7.85(dd)	8.2(d)	7.4-7.7(m)
6	8.9 (d)	7.6 (dd)	8.0(d)	7.5-7.7(m)
7	8.9 (d)	7.4 (dd)	7.85(d)	

To account for the above observations we advance the following two alternative hypothesis: a) The sulfur delocalizes directly the charge through the space[15] and then, the usual way of charge delocalization by the cross-conjugated π-system only operates as a less efficient mechanism. b) A *peripheral ring current* involving 14-π electrons is established through the space having three interruptions in the σ-framework, in such a way that would resemble a trishomoaromatic system in which the discontinuities in the π-system would result from lack of σ-bonding rather than from the insertion of methylene groups. The existence of such a *ring current* should be expected to result in the shielding of the four central carbons and the deshielding of the peripherical protons as in fact it is observed. To our opinion, the first hypothesis (a) hardly might account for the observed proton deshielding. Work is in progress for further insight in the structural features of the intriguing tris(2-thienyl)methyl carbenium ion **7**.

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