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Analysis of substituent effects on the carbon-13 and oxygen-17 NMR chemical shifts of some phenylthiophen-2′-ylmethanones by linear free energy relationships

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ABSTRACT: The ^{13}C chemical shifts of the title compounds (**1**) were determined in $CDCl_3$ and in CD_3OD as well as in D_2SO_4 solutions. Moreover ^{17}O chemical shifts of **1** in $CDCl_3$ were measured. The SCS (substituent-induced chemical shift) values were analyzed by means of linear free energy (LFE) relationships and also by cross-correlations with those of both the corresponding 5-substituted 2-acetylthiophenes (**2**) and 4-substituted acetophenones (**3**). The ^{13}C SCS values indicate a transmission pattern of the substituent effect which is more complex than those observed in **2** and **3**. On the other hand, the ^{17}O SCS values are more significant and reliable indicators of the transmission of the electronic effects on to the carbonyl group of **1**, clearly underlining the different propensities of the phenyl and the thiophen-2′-yl groups in accomplishing such a transmission. Some apparent discrepancies observed between protonation and ^{17}O NMR data of compounds **1, 2** and **3** are also discussed.

KEYWORDS: phenylthiophen-2′-ylmethanones; ^{13}C NMR; ^{17}O NMR; substituent effects; linear free energy relationships

INTRODUCTION

Phenylthiophen-2′-ylmethanone (**1hh**) and other aromatic ketones are important compounds in several respects. Thus, **1hh** itself finds applications (*i*) in pharmacology[1] being, for instance, more efficient than aspirin as an anti-aggregating agent[2] (*ii*) as a component of polymerization catalysts[3] or (*iii*) as a crystal for generating higher harmonics in Nd:YAG lasers.[4] Recently a photophysical study[5] indicated that **1hh** also behaves as an efficient triplet sensitizer but the typical n,π* triplet reactivity of aryl ketones is partially lost. Conformational studies[6] have shown that the sulfur atom of **1hh** is on the same side as the carbonyl group, with which the thiophen-2′-yl ring is almost coplanar.

Recently, in the framework of our research on the electron-density distribution in ArCOY compounds, we have investigated the protonation of some phenylthiophen-2′-ylmethanones,[7] pointing out that the substituent effects are better transmitted through the thiophene rather than through the benzene ring, thus enlightening the greater conjugative ability of the former ring.[8] Protonation equilibria of the carbonyl group are very sensitive to changes in π-conjugation induced by a substituent and/or by conformational variations; since the electron-density distribution and hence the extent of π-conjugation in unsaturated molecules can be successfully estimated by means of NMR spectroscopy,[9] we thought it of interest to analyze substituent effects on both ^{13}C and ^{17}O chemical shifts of the carbonyl group of some substituted phenylthiophen-2′-ylmethanones (**1**). Indeed, mono- and disubstituted benzenes[10] and also heterocycles[11,12] have been widely used as models for studying ^{13}C and, when possible,^{17}O substituent-induced chemical shifts (SCS). The analysis of the SCS values of endocyclic carbon atoms by using both single-parameter [Hammett equation, Eqn. 1] or dual substituent parameter [DSP, Eqn. 2] equations [the DSP equation[9a] separates substituent effects into polar (σ_I) and resonance (σ_R) components and uses one of the four different resonance scales (σ_R^+, σ_R^-, σ_R^{BA} and σ_R) depending on the electronic demand

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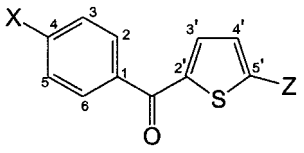
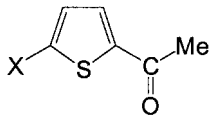


1



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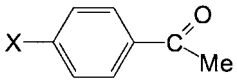


3

1ah: X = NO_2; Z = H
1bh: X = Br; Z = H
1ch: X = Cl; Z = H
1dh: X = Me; Z = H
1eh; X = MeO; Z = H

1hh: X = Z = H

1ha: X = H; Z = NO_2
1hb: X = H; Z = Br
1hc: X = H; Z = Cl
1hd: X = H; Z = Me
1he: X = H; Z = MeO

at the reaction or measuring site], owing to the complexity of effects which affect the ^{13}C SCS values[13] often gave bad results:

$$SCS = \rho\sigma + i \quad (1)$$

$$SCS = \rho_I\sigma_I + \rho_R\sigma_R + i \quad (2)$$

In contrast, SCS values of exocyclic atoms have been mainly expressed by correlation with a DSP equation, obtaining satisfactory results.[9] However, in many aromatic and heteroaromatic systems appropriate cross-correlations gave good results[14] allowing the dependence of SCS on structure to be described. Thus, in this study, together with Eqns 1 and 2, we used appropriate cross-correlations. In fact, it has been shown[9b,d] that this kind of study furnishes interesting information for monitoring the nature of the interactions between the aromatic (or heteroaromatic) ring and the probe (in this case carbonyl). The substituents studied range from the strongly electron-withdrawing nitro group to the strongly electron-donating methoxy group. The influence of the solvent on the transmission of the substituent effect on the probe group has also been evaluated, the solvents used ranging from $CDCl_3$, for which interactions with the carbonyl should be of little importance, to CD_3OD or to D_2SO_4 solutions, for which strong interactions with the probe group are expected. CD_3OD and D_2SO_4 (as we have recently pointed out[7] in D_2SO_4 all the phenylthiophene-2′-ylmethanones are fully protonated) solutions provide spectra of unprotonated (series **1**) and protonated (series $\mathbf{1H}^+$) compounds at the carbonyl group, respectively. Previously we examined NMR and protonation data for both substituted 2-acetylthiophenes **2**[15] and acetophenones **3**.[9d] Now the phenylthiophen-2′-ylmethanones (**1**) appear promising substrates to evaluate the competitive steric and electronic requirements of phenyl and thiophen-2′-yl rings.

RESULTS AND DISCUSSION

The ^{13}C and ^{17}O substituent-induced chemical shift [SCS = δ_X (or δ_Z) $-\delta_H$] values of **1** and the ^{13}C SCS values of $\mathbf{1H}^+$ are reported in Tables 1 and 2, positive signs denoting nuclear deshielding with respect to the parent compound **1hh** (X = Z = H) and *vice versa*.

First, in order to evaluate the solvent effect, the ^{13}C SCS values of **1** in CD_3OD were cross-correlated with those in $CDCl_3$. Endocyclic carbon atoms of both rings (also those *meta* or *meta*-like with respect to the substituent or to the carbonyl group, *i.e.* the bridge for the transmission of the electronic effect) gave slope values close to unity with excellent statistical results (see Table 3, lines 2–9), showing that the substituent effect considered is much the same in both solvents. By contrast, the cross-correlation between SCS values for the carbonyl carbon in CD_3OD and in $CDCl_3$ (Table 3, line 1: $\beta = 1.35$, $r = 0.950$) indicates a larger solvent effect on the carbonyl in CD_3OD than in $CDCl_3$, in agreement with the higher electrophilicity of methanol with respect to chloroform [the relevant constants for the undeuterated solvents being E(MeOH) = 14.94 and $E(CHCl_3) = 3.17$[16]] and with some differences in the modulation of the substituent effects (compare the correlation coefficient with those calculated for the endocyclic carbon atoms). These results indicate that any solvent effect is essentially localized at the level of the carbonyl group and does not influence the electron density on the aromatic rings. We had previously shown that in 2-acetylthiophenes (**2**) the C═O···$DOCD_3$ interactions (increasing the electronic requirement of the carbonyl) moderately affected, with respect to $CDCl_3$, the electron density at C-2 ($\beta = 1.14$) and C-3 ($\beta = 1.26$) of the thiophene ring, too.[15] The different behavior of compounds **1** here is probably attributable to the fact that the carbonyl group effect can be distributed (and thus 'diluted') on to two aromatic rings; accordingly, the ^{13}C chemical shift in $CDCl_3$ of the carbonyl carbon atom of **1hh** (188.91 ppm) is lower than that of 2-acetylthiophene (190.59 ppm).[8a]

The effect of the X- or Z-substituents on the carbonyl ^{13}C NMR chemical shift values in CD_3OD was analyzed by means of the single-parameter linear free energy (LFE) correlation of Eqn. 1 (Table 3, lines 10–19), using the σ_p set of substituent constants (the σ_p^+ set giving on the whole similar but statistically worse results). While the carbon atoms of the unsubstituted ring (thiophen-2′-yl for **1ah–eh,hh** and phenyl for **1ha–he,hh**) generally

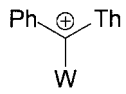
Table 1. ^{13}C NMR substituent chemical shifts [SCS = δ_X (or δ_Z) $-\delta_H$] for **1** in CD_3OD and **1H**$^+$ in D_2SO_4 (figures in parentheses); positive values correspond to a deshielding effect, with respect to the parent **1hh**

Compound	X or Z	C=O	C-1	C-2	C-3	C-4	C-2′	C-3′	C-4′	C-5′
1ah	NO_2	−3.04	4.69	1.04	−4.86	16.86	−0.45	0.74	0.38	1.17
		(−2.12)	(4.79)	(0.49)	(−5.17)	(12.10)	(1.45)	(1.74)	(1.33)	(5.14)
1bh	Br	−1.25	−1.08	1.76	3.31	−5.37	−0.34	0.04	0.12	0.31
		(−1.29)	(−1.33)	(1.11)	(3.17)	(−3.13)	(−0.08)	(−0.26)	(0.17)	(0.52)
1ch	Cl	−1.39	−1.49	1.68	0.28	6.20	−0.31	0.01	0.11	0.27
		(−1.51)	(−1.73)	(1.25)	(0.48)	(7.68)	(−0.06)	(−0.28)	(0.19)	(0.40)
1dh[a]	Me	−0.20	−2.73	0.27	0.63	11.15	0.15	−0.30	−0.08	−0.31
		(−1.09)	(−2.81)	(0.66)	(0.95)	(14.38)	(−0.21)	(−1.17)	(−0.45)	(−1.95)
1eh[b]	MeO	−1.20	−7.75	2.58	−14.72	31.41	0.21	−0.77	−0.18	−0.80
		(−3.85)	(−6.90)	(4.44)	(−13.78)	(29.17)	(−0.51)	(−2.77)	(−0.84)	(−4.05)
1hh[c]	H	189.98	139.31	130.12	129.62	133.58	144.43	136.68	129.40	136.09
		(191.84)	(128.90)	(132.21)	(129.80)	(138.80)	(133.67)	(150.99)	(133.42)	(156.64)
1ha	NO_2	−0.94	−1.75	0.34	0.36	1.02	4.23	−2.37	0.29	22.60
		(5.77)	(−0.82)	(1.98)	(0.67)	(3.36)	(3.48)	(−3.17)	(−3.04)	(7.94)
1hb	Br	−1.35	−0.83	−0.04	0.15	0.26	1.89	0.38	3.64	−11.88
		(−2.47)	(−0.55)	(−0.30)	(0.14)	(0.11)	(1.16)	(0.62)	(3.92)	(−7.25)
1hc	Cl	−1.18	−0.91	−0.05	0.14	0.24	−0.89	−0.18	−0.01	4.83
		(−1.90)	(−0.66)	(−0.33)	(0.10)	(0.05)	(0.13)	(0.90)	(0.38)	(7.40)
1hd[d]	Me	−0.20	0.09	−0.08	−0.01	−0.18	−2.09	0.97	−1.00	16.46
		(−3.99)	(0.07)	(−0.87)	(−0.21)	(−1.15)	(−2.24)	(1.08)	(0.61)	(22.60)
1he[e]	MeO	−0.26	−0.08	−0.28	0.00	−0.50	−13.81	1.80	−21.81	41.13
		(−11.10)	(−0.04)	(−2.38)	(−0.44)	(−3.24)	(−2.58)	(3.56)	(−13.95)	(39.49)

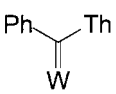
[a] *C*H$_3$ 21.59 (21.19) ppm.
[b] *C*H$_3$O 58.06 (56.56) ppm.
[c] Chemical shifts (ppm) for the parent systems **1hh** [relative to CD_3OD (49.00 ppm with respect to TMS)] and **1H**$^+$**hh** [relative to trimethylammonium (45.35 ppm with respect to TMS)].
[d] *C*H$_3$ 15.93 (17.00) ppm.
[e] *C*H$_3$O 61.22 (64.06) ppm.

provided significant correlations (lines 10–17), SCS values for endocyclic carbon atoms of the substituted ring (phenyl for **1ah–eh,hh** and thiophen-2′-yl for **1ha–he,hh**) were found not to correlate significantly with σ_p (data not reported), except for C-1 (line 18) and C-3′ (line 19). The good correlation *versus* σ_p^+ of the C-1 SCS values for compounds **1ah–eh,hh** (Table 3, line 18) matches well previous results[9b,10,17] for 4-substituted-acetophenones **3** [$SCS_{C-1(3)} = -1.17 \pm 0.36 + (8.61 \pm 0.45)\sigma_p^+$, $n = 8$, $r = 0.989$]. Moreover, a very good cross-correlation holds between the SCS values above and those relevant to the *para*-carbon atom of monosubstituted benzenes (PhX)[10] [$SCS_{C-1(\mathbf{1ah–eh,hh})} = -0.22 \pm 0.25 + (0.89 \pm 0.06)SCS_{C-4(PhX)}$, $n = 6$, $r = 0.992$], the slope of which testifies to some attenuation of the ^{13}C sensitivity to the substituent effect played by the bonded CO—2′-Th group with respect to H itself.

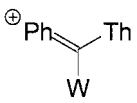
The ^{13}C chemical shift dependence on substituent in a distant aromatic or heteroaromatic ring is not a surprising result. Indeed, it has been found that in compounds such as Z-α-(*p*-substituted phenyl)-β-(5-substituted thiophen-2-yl)acrylonitriles,[18] thiophene and furan chalcone analogues,[19] *N*-benzylideneanilines,[20] azobenzenes,[21] styrenes[21] and 2- and 3-thiophenecarboxanilides[22] containing two aromatic rings, the ^{13}C chemical shift values of the *para*-carbon atom of an unsubstituted ring are affected by electronic effects of remote substituents showing good correlations with substituent constants. Thus the trend seems to emerge that remote substituents cause chemical shift variations at ring carbon atoms that can be linearly correlated by the Hammett equation, in contrast with the effects exerted by near substituents. Negative slopes (lines 10 and 14) most likely reflect the contribution of the resonance structure **A**, which justifies



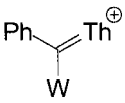
A : W = O$^-$
AH$^+$: W = OH



B : W = O
BH$^+$: W = $^+$OH



C : W = O$^-$
CH$^+$: W = OH



D : W = O$^-$
DH$^+$: W = OH

Table 2. ^{13}C and ^{17}O NMR substituent chemical shifts [SCS = δ_X (or δ_Z) $-\delta_H$] for 1 in $CDCL_3$; positive values correspond to a deshielding effect with respect to the parent **1hh**

		^{13}C									^{17}O:
Compound	X or Z	C=O	C-1	C-2	C-3	C-4	C-2′	C-3′	C-4′	C-5′	CO
1ah[a]	NO_2	−1.96	4.48	0.76	−4.72	17.54	−0.31	0.85	0.47	1.27	13.4
1bh	Br	−1.17	−1.28	1.55	3.35	−4.99	−0.45	−0.04	0.14	0.38	6.5
1ch	Cl	−1.34	−1.74	1.42	0.35	6.43	−0.43	−0.09	0.11	0.32	−1.1
1dh[b]	Me	−0.33	−2.72	0.22	0.69	10.77	0.16	−0.39	−0.10	−0.39	−6.2
1eh[c]	MeO	−1.39	−7.48	2.43	−14.72	30.83	0.20	−0.85	−0.19	−0.79	−10.7
1hh[d]	H	188.91	138.80	129.83	129.07	132.93	144.29	135.52	128.62	134.88	515.8
1ha[e]	NO_2	−0.86	−2.01	0.16	0.46	1.27	3.88	−2.67	−0.03	22.20	20.9
1hb	Br	−1.23	−0.80	−0.12	0.14	0.25	1.44	0.15	3.18	−11.19	2.6
1hc	Cl	−1.08	−0.87	−0.16	0.12	0.20	−1.40	−0.44	−0.48	5.85	−1.1
1hd[f]	Me	−0.34	0.07	−0.19	−0.12	−0.34	−2.25	0.42	−1.23	16.19	−9.4
1he[g]	MeO	−0.54	−0.10	−0.36	−0.09	−0.63	−13.61	1.12	−21.76	40.85	−22.4

[a] NO_2 576.0 ppm.
[b] CH_3 22.29 ppm.
[c] CH_3O 56.14 ppm; CH_3O 62.4 ppm.
[d] ^{13}C and ^{17}O chemical shifts (ppm) for the parent system **1hh** [relative to $CDCl_3$ (77.00 ppm with respect to TMS) or the external 1,4-dioxane (0.0 ppm), respectively].
[e] NO_2 574.2 ppm.
[f] CH_3 16.08 ppm.
[g] CH_3O 61.13 ppm; CH_3O 60.8 ppm.

the polarization of the π-electrons of the unsubstituted ring due to electronic effects on the substituted ring.

The good or poor success of the above correlations could indicate that the interactions of the substituent with the relevant probe atom in the ground and excited states are similar or different, respectively.[23] On the other hand, the occurrence of excellent cross-correlations (see discussion above and Table 3, lines 2–9) on going from chloroform to methanol also for those ring carbon atoms that give non-linear Hammett plots indicates that the substituent–ring–probe interactions in the ground and excited states are scarcely affected by the solvent employed. For this reason, we have reported (Table 3, lines 10–19) only correlations for data in CD_3OD, as data in $CDCl_3$ gave practically identical figures.

As the results of LFE correlations were on the whole considered unsatisfactory, SCS values of **1** were compared with SCS values of 4-substituted acetophenones (**3**)[10,17] and of 5-substituted 2-acetylthiophenes (**2**)[15] obtaining (see Table 3, lines 20–27) excellent statistical results. Slope values close to unity (β = 0.94–1.09) were calculated for the above cross-correlations. Therefore, on going from **1** to **3** (*i.e.* replacing the thiophen-2′-yl ring with a methyl group) or from **1** to **2** (*i.e.* replacing the phenyl ring with a methyl group), significant variations in the transmission of substituent effects through the substituted ring are not observed, an outcome that can be related (*i*) to the low conjugation existing between the unsubstituted ring and the carbonyl group in compounds **1** or (*ii*) to the fact that on going from **1** to **3** or from **1** to **2** interactions between the substituent and the relevant probe atom in the ground and in the excited state are similar.

Concerning the effect of substituents on the carbonyl carbon (C-α), the SCS values reported in Table 1 show that all the substituents exert a shielding effect on the ^{13}C chemical shift, whatever their polar effects, much as already observed, both qualitatively and quantitatively, *e.g.*, for 4-substituted acetophenones **3**.[9b,10,17] Here, though, at variance with compounds **3**, poor correlations are obtained not only for the single-parameter but also for the DSP analysis, the limited number of experimental points most likely playing a role. On the other hand, it is very interesting that the (C-α) SCS values of **1ah–eh,hh** gave an excellent correlation *versus* the corresponding data for **3** (Table 3, line 20). In contrast, a similar correlation between the SCS values of **1ha–he,hh** and **2** proved very poor (data not reported; $r < 0.2$); these results seem to indicate that the conformational differences between **1ha–he,hh** and the corresponding 2-acetylthiophenes **2** play a more important role than those between **1ah–eh,hh** and the corresponding acetophenones **3**. This appears in contrast with the fact that the C-α ^{13}C chemical shift of compound **1hh** (188.91 ppm) is much more similar to that of 2-acetylthiophene (190.59 ppm)[8a] than to that of acetophenone (198.01 ppm).[10,17]

Protonation of the carbonyl group in **1** causes a shielding (*ca* 10 ppm) for the carbon atoms directly linked to it (C-1 and C-2′) and a deshielding for the other endocyclic carbon atoms. The chemical shift variations observed agree with the expected increase in the electron-withdrawing effect of the carbonyl group after protonation, which makes structures $\mathbf{CH}^+$ and $\mathbf{DH}^+$ more important for $\mathbf{1H}^+$ than the corresponding **C** and **D** for **1**. As a consequence, the electron density decreases on C-2, C-3, C-4, C-3′, C-4′ and C-5′ and increases for C-1 and C-2′.

As the thiophen-2′-yl ring conjugates with the carbonyl

Table 3. Statistical results (Hammett equations and cross-correlations) for the ^{13}C and ^{17}O SCS values of **1**[a]

Line	Probe atom	Series	Probe atom (or σ)[b]	Series	$\rho \pm s_\rho$ (or $\beta \pm s_\beta$)	$i \pm s_i$	n	r	C.L.> (%)
1	$C_{(C=O)}$	**1**[c]	$C_{(C=O)}$	**1**[d]	1.35 ± 0.14	0.23 ± 0.14	11	0.950	99.9
2	C-1	**1**[c]	C-1	**1**[d]	1.03 ± 0.01	0.08 ± 0.04	11	0.999	99.9
3	C-2	**1**[c]	C-2	**1**[d]	1.06 ± 0.03	0.10 ± 0.03	11	0.997	99.9
4	C-3	**1**[c]	C-3	**1**[d]	1.00 ± 0.01	-0.01 ± 0.02	11	0.999	99.9
5	C-4	**1**[c]	C-4	**1**[d]	1.01 ± 0.01	-0.07 ± 0.11	11	0.999	99.9
6	C-2′	**1**[c]	C-2′	**1**[d]	1.03 ± 0.01	0.14 ± 0.06	11	0.999	99.9
7	C-3′	**1**[c]	C-3′	**1**[d]	1.03 ± 0.08	0.19 ± 0.07	11	0.973	99.9
8	C-4′	**1**[c]	C-4′	**1**[d]	1.01 ± 0.01	0.13 ± 0.06	11	0.999	99.9
9	C-5′	**1**[c]	C-5′	**1**[d]	1.01 ± 0.01	-0.17 ± 0.11	11	0.999	99.9
10	C-2′	**1ah–eh,hh**[c]	σ_p		-0.66 ± 0.15	-0.03 ± 0.06	6	0.906	99.0
11	C-3′	**1ah–eh,hh**[c]	σ_p		1.23 ± 0.19	-0.22 ± 0.07	6	0.957	99.0
12	C-4′	**1ah–eh,hh**[c]	σ_p		0.50 ± 0.02	-0.01 ± 0.01	6	0.995	99.9
13	C-5′	**1ah–eh,hh**[c]	σ_p		1.70 ± 0.15	-0.13 ± 0.06	6	0.984	99.9
14	C-1	**1ha–he,hh**[c]	σ_p		-1.78 ± 0.29	-0.33 ± 0.11	6	0.951	99.0
15	C-2	**1ha–he,hh**[c]	σ_p		0.49 ± 0.09	-0.09 ± 0.03	6	0.933	99.0
16	C-3	**1ha–eh,hh**[c]	σ_p		0.36 ± 0.04	0.06 ± 0.02	6	0.972	99.9
17	C-4	**1ha–he,hh**[c]	σ_p		1.34 ± 0.06	-0.04 ± 0.02	6	0.996	99.9
18	C-1	**1ah–eh,hh**[c]	σ_p+		7.41 ± 0.91	-1.37 ± 0.44	6	0.971	99.9
19	C-3′	**1ha–he,hh**[c]	σ_p		-3.53 ± 0.50	0.59 ± 0.19	6	0.962	99.9
20	$C_{(C=O)}$	**1ah–eh,hh**[d]	$C_{(C=O)}$	**3**[d]	1.09 ± 0.07	0.02 ± 0.08	6	0.992	99.9
21	C-1	**1ah–eh,hh**[d]	C-1	**3**[d]	1.07 ± 0.02	-0.06 ± 0.06	6	0.999	99.9
22	C-2	**1ah–eh,hh**[d]	C-2	**3**[d]	1.08 ± 0.11	0.14 ± 0.13	6	0.980	99.9
23	C-4	**1ah–eh,hh**[d]	C-4	**3**[d]	1.02 ± 0.01	-0.13 ± 0.05	6	0.999	99.9
24	C-2′	**1ha–he,hh**[d]	C-2	**2**[c]	0.94 ± 0.03	0.05 ± 0.17	6	0.998	99.9
25	C-3′	**1ha–he,hh**[d]	C-3	**2**[c]	0.97 ± 0.15	0.43 ± 0.19	6	0.957	99.0
26	C-4′	**1ha–he,hh**[d]	C-4	**2**[c]	0.99 ± 0.01	0.13 ± 0.09	6	0.999	99.9
27	C-5′	**1ha–he,hh**[d]	C-5	**2**[c]	1.02 ± 0.02	0.57 ± 0.35	6	0.999	99.9
28	$O_{(C=O)}$	**1ah–eh,hh**[d]	σ_p+		15.76 ± 2.80	0.37 ± 1.10	6	0.961	99.9
29	$O_{(C=O)}$	**1ha–he,hh**[d]	σ_p+		26.92 ± 1.30	-1.47 ± 0.62	6	0.995	99.9

[a] ρ, Susceptibility constant; β, slope of the cross-correlation; i, intercept of the regression line; s_ρ, s_β and s_i, standard deviations of ρ, β and i, respectively; n, number of data points; r, correlation coefficient; C.L., confidence level.
[b] Substituent constants from Ref. 26; σ_p, NO_2 (+0.81), Br (+0.22), Cl (+0.22), H (0), Me (−0.14), MeO (−0.28); σ_p+, NO_2 (+0.81); Br (+0.15), Cl (+0.11), H (0), Me (−0.31), MeO (−0.78).
[c] Solvent: CD_3OD.
[d] Solvent: $CDCl_3$.

group more efficiently than the phenyl ring,[8] the deshielding effect on C-3′, C-4′ and C-5′ is more pronounced than on C-2, C-3 and C-4 on going from **1** to $\mathbf{1H}^+$. Furthermore, for both rings the deshielding is, as expected, greater for the carbon atoms (C-2, C-4 and C-3′, C-5′) conjugated with the protonated carbonyl group than for the unconjugated ones (C-3 and C-4′).

A correlation of the SCS values for $\mathbf{1H}^+$ with those for **1** (see Table 4, lines 1–13) allows us to analyze the influence of the carbonyl protonation on the transmission of substituent effects. For compounds bearing the substituent on the phenyl ring (**1ah–eh,hh**) bad correlations resulted (data not reported; $r < 0.9$) for C-2 and C-2′, whereas for the other endocyclic carbon atoms (C-1, C-3, C-4, C-3′, C-4′ and C-5′) good correlations ($r \geq 0.98$) were obtained. It is interesting to observe that slope values slightly smaller than unity for phenyl carbon atoms (C-1, C-3 and C-4: $\beta = 0.86$–0.95) and significantly higher than unity for thiophen-2′-yl carbon atoms (C-3′, C-4′ and C-5′: $\beta = 3.0$–4.6) were calculated, indicating that protonation appreciably alters (*i.e.* enhances) the transmission of the substituent effects only through the unsubstituted thiophen-2′-yl ring. Analogous indications derive from the analysis of compounds bearing the substituent on the thiophen-2′-yl ring (**1ha–he,hh**): a bad correlation (data not reported; $r < 0.9$) relative to C-2′ was again obtained, whereas for the other endocyclic carbon atoms good (C-1, C-2, C-4, C-3′ and C-4′: $r > 0.96$) or acceptable (C-3 and C-5′: $r \approx 0.92$) correlations were obtained. Slope values slightly smaller (C-4′ and C-5′: $\beta = 0.65$ and 0.83) or higher (C-3′: $\beta = 1.5$) than unity were calculated for endocyclic carbon atoms of the thiophen-2′-yl ring (the substituted ring). In contrast, very high slope values were observed for endocyclic carbon atoms (C-2, C-3 and C-4: $\beta = 2.4$–6.9) of the phenyl ring (the unsubstituted ring) whereas for C-1 a value lower than unity was obtained ($\beta = 0.52$).

The SCS values of $\mathbf{1H}^+$**ha–he,hh** were compared with those of $\mathbf{2H}^+$: excellent correlations (see Table 4, lines 15–16; $r > 0.99$) for C-4′ and C-5′ and bad correlations

Table 4. Statistical data[a] for the cross-correlations, for the single-parameter and DSP analysis of ^{13}C SCS values of **1H**$^+$ in D_2SO_4

Line	Probe atom	Series	Probe atom (or σ)[b]	Series	$\rho \pm s_\rho$ (or $\beta \pm s_\beta$)	$i + s_i$	n	r	C.L.> (%)
1	C-1	**1H**$^+$**ah–eh,hh**	C-1	**1ah–eh,hh**[c]	0.94 ± 0.04	-0.02 ± 0.16	6	0.996	99.9
2	C-3	**1H**$^+$**ah–eh,hh**	C-3	**1ah–eh,hh**[c]	0.95 ± 0.02	0.05 ± 0.16	6	0.999	99.9
3	C-4	**1H**$^+$**ah–eh,hh**	C-4	**1ah–eh,hh**[c]	0.86 ± 0.09	1.36 ± 1.44	6	0.978	99.9
4	C-3′	**1H**$^+$**ah–eh,hh**	C-3′	**1ah–eh,hh**[c]	2.98 ± 0.18	-0.32 ± 0.08	6	0.993	99.9
5	C-4′	**1H**$^+$**ah–eh,hh**	C-4′	**1ah–eh,hh**[c]	3.75 ± 0.25	-0.15 ± 0.05	6	0.991	99.9
6	C-5′	**1H**$^+$**ah–eh,hh**	C-5′	**1ah–eh,hh**[c]	4.59 ± 0.26	-0.48 ± 0.16	6	0.993	99.9
7	C-1	**1H**$^+$**ha–he,hh**	C-1	**1ha–he,hh**[c]	0.52 ± 0.07	-0.03 ± 0.06	6	0.965	99.9
8	C-2	**1H**$^+$**ha–he,hh**	C-2	**1ha–he,hh**[c]	6.93 ± 0.52	-0.19 ± 0.10	6	0.989	99.9
9	C-3	**1H**$^+$**ha–he,hh**	C-3	**1ha–he,hh**[c]	2.42 ± 0.49	-0.21 ± 0.08	6	0.927	99.0
10	C-4	**1H**$^+$**ha–he,hh**	C-4	**1ha–he,hh**[c]	4.07 ± 0.42	-0.71 ± 0.21	6	0.979	99.9
11	C-3′	**1H**$^+$**ha–he,hh**	C-3′	**1ha–he,hh**[c]	1.49 ± 0.20	0.35 ± 0.26	6	0.964	99.9
12	C-4′	**1H**$^+$**ha–he,hh**	C-4′	**1ha–he,hh**[c]	0.65 ± 0.09	0.03 ± 0.83	6	0.962	99.9
13	C-5′	**1H**$^+$**ha–he,hh**	C-5′	**1ha–he,hh**[c]	0.83 ± 0.18	1.63 ± 3.80	6	0.916	99.0
14	$C_{(C=O)}$	**1H**$^+$**ha–he,hh**	$C_{(C=O)}$	**2H**$^+$[d]	0.67 ± 0.01	-0.41 ± 0.12	6	0.999	99.9
15	C-4′	**1H**$^+$**ha–he,hh**	C-4	**2H**$^+$[d]	0.89 ± 0.02	0.05 ± 0.16	6	0.999	99.9
16	C-5′	**1H**$^+$**ha–he,hh**	C-5	**2H**$^+$[d]	1.17 ± 0.07	-1.04 ± 1.16	6	0.993	99.9
17	$C_{(C=O)}$	**1H**$^+$**ha–he,hh**	σ_p+		9.99 ± 1.44	-2.25 ± 0.69	6	0.961	99.9
18	$C_{(C=O)}$	**1H**$^+$**ha–he,hh**	σ_I,σ_R+		ρ_I 5.97 ± 1.17 ρ_R^+ 12.45 ± 0.79	-0.36 ± 0.53	6	0.995	99.9

[a] As in Table 3.
[b] Substituent constants from Ref. 26; σ_I, σ_R^+, NO_2 (+0.67, 0.00), Br (+0.47, −0.44), Cl (+0.47, −0.48), H (0, 0), Me (−0.01, −0.30), MeO (+0.30, −1.15).
[c] Solvent: CD_3OD.
[d] Solvent: D_2SO_4.

(data not reported; $r < 0.9$) for C-3′ and C-2′ were observed. The slope value ($\beta = 0.43$) calculated for the latter correlation is the result of the fact that the shielding effect on C-2′ in **2H**$^+$ (*ca* 15 ppm) is reduced in **1H**$^+$**ha–he,hh** (*ca* 6 ppm) as a consequence of the already mentioned possibility, for **1** and/or **1H**$^+$, of transmitting any electronic demand of the carbonyl group on to two aromatic moieties; in other words, the result should reflect the relative abilities of a phenyl and a methyl group to delocalize an adjacent positive charge. Confirmation is provided by the shielding effect measured upon protonation, on the methyl carbon in **2** (*ca* 3.5 ppm) and on C-1 in **1hh** (*ca* 10 ppm).

As far as the carbonyl carbon is concerned, structure **AH**$^+$ accounts for the deshielding observed in **1H**$^+$ with respect to **1** for compounds with strong electron-withdrawing substituents (X or Z = NO_2). In contrast, for compounds with strong electron-donating substituents (X or Z = MeO) an increased relevance of structures **CH**$^+$ (or **DH**$^+$) determines an increase in electron density (and then a shielding) on the carbonyl carbon of **1H**$^+$**eh,he** with respect to **1eh,he**.

The SCS data for the carbonyl carbon of **1H**$^+$**ah–eh,hh** (see Table 1) did not show a simple dependence on substituent effects, as indicated by the poor results (data not reported; $r < 0.4$) obtained by using both single-parameter and DSP equations. In contrast, the corresponding data for **1H**$^+$**ha–he,hh** gave a good result using a single-parameter equation and an excellent result using the DSP equation (Table 4, lines 17 and 18). It is interesting that the value calculated for the ratio of resonance to inductive effect ($\lambda = \rho_R^+/\rho_I$) is practically identical (*ca* 2) with that observed for the carbonyl carbon of protonated **2**[15] and **3**.[10,,17] Both the susceptibility constants (ρ_R^+ and ρ_I) calculated for **1H**$^+$**ha–he,hh** proved very similar to those for **3H**$^+$ and about half of those for **2H**$^+$. This is in a way surprising since a behavior of **1H**$^+$**ha–he,hh** more similar to **2H**$^+$ than to **3H**$^+$ with regard to the transmission of substituent effects on to the carbonyl carbon could have been expected. Probably conjugation of the phenyl ring with the carbonyl carbon atom in **1H**$^+$**ha–he,hh**, although not extensive, is able to modify appreciably the transmission of substituent effects from the thiophen-2′-yl ring to the same carbon. On the other hand, the resemblance in behavior between **1H**$^+$**ha–he,hh** and **3H**$^+$ should be considered fortuitous; in fact, for the former compounds the two aromatic rings cause a kind of saturation effect on the carbonyl carbon atom [as the small variation (<2 ppm) in chemical shift on going from **1hh** (189.98 ppm) to **1H**$^+$**hh** (191.84 ppm) shows], whereas for compounds **3H**$^+$ the size of the above-mentioned susceptibility constants arises from the lower ability of the phenyl ring to conjugate as compared with the thiophen-2′-yl ring.

The ^{17}O chemical shift value of **1hh** (515.8 ppm) compared with those of acetophenone (542.5 ppm[24]) and 2-acetylthiophene (518.6 ppm[8a]) shows that the replace-

ment of a methyl group for a thiophen-2′-yl ring (*i.e.* **3** *vs* **1**) significantly alters the conjugative interactions between carbonyl and aromatic rings; in contrast, substitution of a methyl group for a phenyl ring (*i.e.* **2** *vs* **1**) causes only a meagre electron density variation on the oxygen atom. This confirms that the thiophen-2′-yl ring is appreciably more 'conjugative' than the phenyl ring.

The ^{17}O SCS data for compounds **1** restate that the oxygen atom, because of its sensitivity to variations in electron density[25] is a suitable probe for a study of the substituent effects on the carbonyl electronic distribution; in particular, substituents in *para* or *para*-like positions exert 'normal' effects, as expected on the grounds of the electronic (mesomeric and inductive) properties of the C=O double bond. At variance with the ^{13}C SCS values for the carbonyl carbon atom, the ^{17}O SCS were satisfactorily correlated (see Table 3, lines 28 and 29) by means of a single-parameter equation, by using the σ^+ scale of substituent constants.[26] The different behavior shown by the two SCS data series (^{17}O and ^{13}C) is consistent with the resonance structures **B–D**, highlighting the non-conjugative nature of the carbonyl carbon atom and, in contrast, a conjugation of the oxygen atom with the aromatic rings which is fairly strong, as judged by the large resonance susceptibility constants. Needless to say, very bad results are obtained by ^{17}O *versus* ^{13}C cross-correlations for both the **1ah–eh,hh** and **1ha–he,hh** series, as an evident proof that the two series of SCSs do not imply a common interaction mechanism[23]: *i.e.* for **1**, the electron excitation energy term in the Karplus–Pople equation[27] does not obey the Hammett equation. Nevertheless, the satisfactory correlations obtained for ^{17}O SCS values seem to indicate that the electron excitation term plays a more important role in determining the entity of ^{13}C than that of ^{17}O chemical shifts.

Moreover, interesting information can be obtained from the comparison between the susceptibility constants of the SCS *versus* σ^+ plots for **2** and **3** ($\rho^+_2/\rho^+_3 = 1.7$) and between those for **1ha–he,hh** and **1ah–eh,hh** ($\rho^+_Z/\rho^+_X = 1.7$); these ratios confirm the higher ability of the thiophen-2′-yl ring to transmit substituent effects in comparison with the phenyl ring and furthermore indicate that the relative abilities are not significantly influenced by the nature [intermolecular (**2** *vs* **3**) or intramolecular (**1ha–he,hh** *vs* **1ah–eh,hh**)] of the competition. In this regard, it should be recalled that protonation equilibria for the same series of compounds had furnished ratio values showing a somewhat different balance: ρ^+_Z/ρ^+_X (2.2) $>\rho^+_2/\rho^+_3$ (1.7).[7] This difference can surely be related to the fact that ^{17}O NMR data measure the intrinsic basicity of the oxygen atom, whereas protonation constants measure differences in energy levels between the base and its conjugated acid. Hence, in the latter case at least two factors should be accounted for, *viz.* the variation of solvation effects on going from the base to its conjugated acid and the levelling effect exerted by the thiophen-2′-yl group on the transmission of substituent effects through the phenyl ring which cause a lowering of ρ^+_X with respect to ρ^+_3.

CONCLUSIONS

The occurrence of excellent cross-correlations between ^{13}C SCS data collected in chloroform and methanol seems to indicate that solvation of a carbonyl group does not determine a significant variation of the conformation of **1**. In addition, the excellent cross-correlations between ^{17}O SCS data for **1ah–eh,hh** and the corresponding acetophenones **3** seem to indicate that the shielding effect observed in the ^{17}O chemical shifts on going from acetophenone to **1hh** should be ascribed to the different electronic effect of the thiophen-2-yl ring with respect to the methyl group rather than to a variation in torsion angle between the phenyl ring and the carbonyl moiety. In contrast, the bad cross-correlations between ^{13}C SCS data for **1ha–he,hh** and the corresponding 2-acetylthiophenes **2** seem to indicate that the absence of significant variations in ^{17}O chemical shift on going from 2-acetylthiophene to **1hh** should be ascribed to an increase in torsion angle between the thiophen-2′-yl system and the carbonyl moiety. In fact, such a variation in torsion angle should cause[28] a deshielding of the carbonyl oxygen, which in this case is counter-balanced by the shielding effect due to replacement of the methyl group for the phenyl ring. Although the carbonyl oxygen ^{17}O NMR chemical shifts are more suitable than the carbonyl carbon ^{13}C shifts in order to quantify the transmission of the substituent electronic effects on to the probe group in phenylthiophen-2′-ylmethanone derivatives, the whole of the results obtained testify to the utility of multiple probe atom NMR studies. The data collected confirm that the carbonyl group (COR, COAr), unlike other COY groups (COOR; $CONH_2$), is capable of through conjugation with a directly bonded aromatic or heteroaromatic ring, the extent of conjugation being related to the particular nature of the aromatic/heteroaromatic system.[8a,9,10,15,17,29]

EXPERIMENTAL

Materials. Compounds **1** were prepared according to the general method (Friedel–Crafts acylation) reported previously[30] and the melting-points agree with those given in the literature.

^{13}C and ^{17}O NMR Measurements. ^{13}C NMR spectra were run at 62.9 MHz on a Bruker AC-250 E pulsed Fourier transform spectrometer. Acquisition parameters were spectral width 16K, 64K data points, 45° pulse angle and quadrature phase detection. Chemical shift values were measured from fully decoupled spectra. Peak

assignment was performed by considering the effects of substituents on chemical shifts and occasionally by using off-resonance decoupled or proton coupled spectra. A concentration of 0.3–0.4 mol dm^{-3} in substrate was used for the sample solutions. Spectra of $\mathbf{1H}^+$ and **1** were measured in D_2SO_4 (internal standard: trimethylammonium ion) and in CD_3OD or $CDCl_3$ (internal standard: the solvent used) solutions, respectively.

^{17}O NMR spectra were recorded on a Varian VXR-300 pulsed Fourier transform spectrometer at 40.670 MHz; all spectra were acquired at natural abundance for anhydrous $CDCl_3$ solutions. Chemical shifts were referenced to external 1,4-dioxane.[31] Acquisition parameters were spectral width 30 kHz, 2K data points, 90° pulse angle (35 μs pulse width), quadrature phase detection, acquisition times $T_{acq}>5T_2$ and 50 000–150 000 scans. Processing parameters were exponential multiplication of the FIDs by a line-broadening (LB) factor of 10–25 Hz and zero-filling up to 16K,[32] resulting in a digital resolution of 3.7 Hz per point after Fourier transformation.

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