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^{1}H, ^{13}C and ^{17}O NMR study of substituent effects in 4-substituted phenylthiol esters

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ABSTRACT: The ^{1}H and ^{13}C NMR spectra of 4-substituted phenylthiol acetates, benzoates and cinnamates and the ^{17}O NMR spectra of a few thiol acetates were measured. The ^{13}C chemical shifts of C-1 of the thiol esters when correlated with appropriate substituent-induced chemical shifts (SCS) of monosubstituted benzenes reveal an enhancement of substituent effect at C-1. Several good dual substituent parameter (DSP) correlations of ^{13}C chemical shifts with σ_I and σ_R parameters were obtained for the carbons *para* to the substituent and the carbonyl carbons of all the three series of thiol esters display inverse substituent effects, indicating π-polarization of the thiol ester functionality by the dipole of the substituent. © John Wiley & Sons Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; ^{17}O NMR; substituent-induced chemical shifts; σ_I/σ_R correlations; phenylthiol esters

INTRODUCTION

Thiol esters play a vital role in biological systems as acyl carrier proteins.[1] They are also found to be involved in the functioning of oxido reductases, transferases, hydrolases, ligases, lyases and isomerases and are employed as artificial substrates for esterase determination.[1] In view of their biological significance, a number of studies on the bonding and substituent effects in thiol esters, particularly aromatic thiol esters, have been reported employing different techniques, e.g. dipole moment, IR spectra, UV spectra and MO calculations.[1–8] ^{13}C NMR spectra of a limited number of esters of the form R_1COXR_2 (X = O, S, Se and Te)[8] and ^{19}F resonances of 3- and 4-fluorophenylthiol acetates[9] have also been obtained.

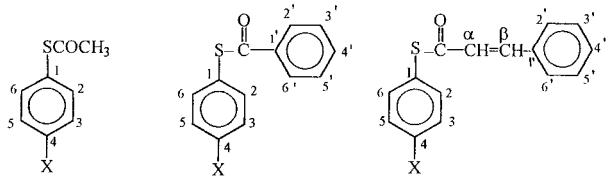
Our recent ^{1}H and ^{13}C NMR study of 4-substituted diphenyl sulphides led to the conclusion that the substituent effects are transmitted from one aryl ring to the other mainly via π-polarization and resonance interactions.[10] Such π-polarization of the carbonyl moiety is possible for thiol esters also, in addition to the classical electronic effects. Prompted by these considerations, we have now studied the ^{1}H and ^{13}C NMR spectra of 4-substituted phenylthiol acetates (Series 1), benzoates (Series 2) and cinnamates (Series 3). ^{17}O NMR spectra of a few representative compounds of Series 1 were also measured and the results are presented in this paper.

EXPERIMENTAL

All the thiol esters employed in this study were prepared by the reaction of the appropriate substituted benzenethiol and acid chloride. The thiol esters were purified by crystallization or distillation under reduced pressure. The b.p./m.p. of the thiol esters for known compounds agreed with the literature values and satisfactory elemental analyses were obtained for previously unreported compounds.

The ^{1}H NMR spectra were measured at 300 MHz (Varian VXR-300) for approximately 0.03 M solutions with TMS as internal reference. Broadband and off-resonance decoupled ^{13}C NMR spectra were obtained at 75 MHz using the same instrument for approximately 0.5 M solutions with TMS as internal reference. The spectra of all compounds were measured in $CDCl_3$. A pulse angle of 37.5° and a repetition time of 3.7 s were used, collecting 32K data points in the quadrature mode at room temperature (20–21 °C). Two-dimensional C/H shift correlated spectra were measured using the standard Varian program HETCOR.

The ^{17}O NMR spectra were recorded at 54.22 MHz on a Varian VXR-400 spectrometer equipped with a 10 mm broadband probe. All spectra were acquired at natural abundance at 75 °C in acetonitrile (Aldrich, anhydrous gold label under nitrogen) containing butan-2-one (1%) as an internal standard. The concentration of the compounds employed in these experiments was typically 0.5 M. The signals were referenced to external



Series 1 Series 2 Series 3

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deionized water at 75 °C. The butan-2-one resonance (558 ppm in acetonitrile) was used as an internal check on the chemical shift measurements for these compounds. The instrumental settings were spectral width 35 kHz, 2K data points, 90° pulse angle (40 μs pulse width), 200 μs acquisition delay and 29 μs acquisition time. Typically 20 000–50 000 scans were required. The spectra were recorded with sample spinning and without lock. The signal-to-noise ratio was improved by applying a 25 Hz exponential broadening factor to the FID prior to Fourier transformation. The data point resolution was improved to 0.01 ppm by zero filling to 8K data points. The reproducibility of the chemical shift data is estimated to be better than 1.0 ppm.

RESULTS AND DISCUSSION

Assignment of the ^{1}H and ^{13}C chemical shifts was based on considerations of peak intensity, peak multiplicity under off-resonance ^{1}H decoupling and with complete ^{1}H coupling, carbon–fluorine couplings and two-dimensional C–H correlations. The ^{1}H chemical shifts for Series 1 and 2 are given in Tables 1 and 2, respectively. In Series 3, the ^{1}H signal assignments were confined to ethylenic protons as the aromatic signals overlap extensively (Table 3). The ^{13}C chemical shifts of C-2′,6′ and C-3′,5′ of Series 3 were not distinguished as they hardly differed. Attached proton test (APT) spectra were used to distinguish the overlapping resonances of proton-bearing and quaternary carbons in some cases. For phenylthiol acetate (**1d**), the chemical shift value of 129.35 ppm was assigned to C-4 in the present study, which differs from that (127.9 ppm) reported by Llabres *et al.*[8] The ^{1}H chemical shifts in Tables 1–3 are considered to be accurate to 0.02 ppm and those for carbon in Tables 4–6 to 0.05 ppm.

Table 1. ^{1}H chemical shifts of 4-substituted phenylthiol acetates (Series 1)

	δ (ppm)			
Substituent	H-2,6	H-3,5	$SCOCH_3$	Others
$N(CH_3)_2$	7.21	6.68	2.35	2.96
OCH_3	7.00	6.63	2.10	3.50
CH_3	7.32	7.20	2.40	2.38
H	7.41	7.41	2.41	7.41 (H-4)
F	7.38	7.10	2.40	—
Cl	7.41	7.31	2.43	—
Br	7.53	7.26	2.41	—
NO_2	7.60	8.25	2.49	—

Correlations of ^{1}H chemical shifts

The ^{1}H chemical shifts of phenylthiol acetates were correlated with dual substituent parameters, σ_I and σ_R°, derived by Bromilow *et al.*,[11] using Taft's equation. Only the H-3,5 protons of Series 1 afford reasonable correlations with σ_I and σ_R° constants ($\rho_I = 0.50$, $\rho_R = 1.91$, $n = 8$).

Lynch correlations of ^{13}C chemical shifts

The ^{13}C chemical shifts of carbons of substituent-bearing aromatic rings of Series 1–3 were correlated with the substituent chemical shift values (SCS) of

Table 2. ^{1}H chemical shifts of 4-substituted phenylthiol benzoates (Series 2)[a]

	δ (ppm)					
Substituent	H-2,6	H-3,5	H-2′,6′	H-3′,5′	H-4′	Others
$N(CH_3)_2$	7.32	6.73	8.02	7.44	7.55	2.97
OCH_3	7.40	6.96	8.05	7.43	7.58	3.80
CH_3	7.44	7.23	8.00	7.38	7.55	2.36
F	7.45	7.15	8.00	7.58	7.65	—
Cl	7.41	7.41	8.00	7.57	7.59	—
Br	7.62	7.35	8.00	7.63	7.47	—
NO_2	7.72	8.30	8.03	7.66	7.58	—

[a] The signals of unsubstituted phenylthiol benzoate were not assigned in view of the complexity of the spectrum.

Table 3. Chemical shifts of H-α and H-β of 4-substituted phenylthiol cinnamates (Series 3)

	δ (ppm)						
Hydrogen	OCH_3	CH_3	H	F	Cl	Br	NO_2
H-α	6.79	6.76	6.80	6.75	6.80	6.90	6.80
H-β	7.64	7.65	7.70	7.65	7.70	7.80	7.90

Table 4. ^{13}C chemical shifts of 4-substituted phenylthiol acetates (Series 1)

	δ (ppm)						
Substituent	C-1	C-2,6	C-3,5	C-4	CO	$SCOCH_3$	Others
$N(CH_3)_2$	112.77	135.65	112.57	151.03	196.49	29.72	40.14
OCH_3	118.61	135.99	114.78	160.58	195.07	29.85	55.24
CH_3	124.39	134.33	129.95	139.61	194.44	30.00	21.24
H	127.87	134.37	129.12	129.35	193.90	30.11	—
F[a]	123.20	136.48	116.43	163.43	193.90	30.01	—
Cl	126.31	135.61	129.41	135.79	193.32	30.15	—
Br	126.89	135.77	132.30	123.99	193.07	30.13	—
NO_2	136.36	134.60	123.90	148.06	191.52	30.52	—

[a] ^nJ(C,F) values: ^1J(C,F) = 250.30 Hz (C-4); ^2J(C,F) = 22.10 Hz (C-3,5); ^3J(C,F) = 8.6 Hz (C-2,6).

monosubstituted benzenes (Lynch correlations[12]) and the results are given in Table 7.

All carbons except C-2,6 afford good correlations. The *b* values in the range 1.30–1.35 obtained for C-1 of Series 1–3 indicate that the fixed thiol ester function (SCOR wherein R = CH_3, C_6H_5 and $CH{=}CHC_6H_5$) significantly enhances the effect of the 4-substituent on the chemical shift of C-1. Similar amplification of the substituent effect at C-1 evident from the *b* values for several fixed substituents having —S— as the point of attachment to the ring in 1,4-disubstituted benzenes has been reported (Table 8).[10] Bromilow *et al.*[15] have discussed the amplification of substituent effect at C-1 in terms of shift charge ratio (SCR) at C-1 where SCR is defined as the ratio of the C_p-SCS value of the *para* substituent X to the substituent induced π-charge at that carbon. Bromilow *et al.*[15] related this to the ρ_R term of DSP correlation for each Y group. Table 7 also lists *b* values for other systems depicted below for comparison.

Table 5. ^{13}C chemical shifts of 4-substituted phenylthiol benzoates (Series 2)

	δ (ppm)									
Substituent	C-1	C-2,6	C-3,5	C-4	CO	C-1′	C-2′,6′	C-3′,5′	C-4′	Others
$N(CH_3)_2$	111.68	136.14	112.74	151.14	191.97	136.86	127.34	128.59	133.29	40.18
OCH_3	117.83	136.59	114.93	160.75	190.92	136.59	127.40	128.68	133.53	55.30
CH_3	123.64	134.88	129.96	139.62	190.35	136.54	127.31	128.57	133.43	21.23
H	127.20	134.97	129.10	129.40	189.92	136.51	127.36	128.63	133.54	—
F[a]	122.55	137.05	116.42	163.71	189.93	136.28	127.38	128.78	133.71	—
Cl	125.76	136.22	129.40	135.87	189.48	134.44	127.42	128.73	133.77	—
Br	126.43	136.46	132.38	124.16	189.33	136.27	127.45	128.75	133.80	—
NO_2	135.91	135.35	123.88	148.19	187.89	136.10	127.58	128.96	134.29	—

[a] ^nJ(CF) values: ^1J(C,F) = 220 Hz (C-4); ^2J(C,F) = 40.1 Hz (C-3,5); ^3J(C,F) = 8.6 Hz (C-2,6).

Table 6. ^{13}C chemical shifts of 4-substituted phenylthiol cinnamates (Series 3)

	δ(ppm)										
Substituent	C-1	C-2,6	C-3,5	C-4	CO	C-α	C-β	C-1′	C-4′	C-2′,6′ and C-3′,5′	Others
OCH_3	118.20	136.19	114.87	160.67	188.87	124.05	141.25	134.04	130.66	128.95, 128.44	55.32
CH_3	124.03	134.52	130.00	137.63	188.33	124.12	141.28	133.98	130.65	128.92, 128.43	21.33
H	127.52	134.50	129.10[a]	129.32[a]	187.78	124.01	141.40	133.86	130.55	128.88, 128.32	—
F[b]	122.82	136.47	116.23	163.28	187.41	123.70	141.57	133.71	130.65	128.80, 128.34	—
Cl	126.03	135.65	129.27	133.71	187.01	123.73	141.79	133.57	130.77	128.88, 128.42	—
Br	126.66	135.86	132.23	123.93	186.86	123.75	141.83	133.71	130.77	128.89, 128.42	—
NO_2	136.37	134.62	123.80	148.00	185.40	123.46	142.88	133.62	131.21	128.53, 129.02	—

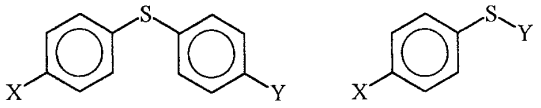
[a] May be reversed.
[b] ^nJ(C,F) values: ^1J(C,F) = 250.1 Hz (C-4); ^2J(C,F) = 22.1 Hz (C-3,5); ^3J(C,F) = 8.6 Hz (C-2,6).

Table 7. Lynch correlations of ^{13}C chemical shifts with benzene SCS values

Series	Atom	Benzene SCS	slope, b	Intercept (ppm) Calculated	Intercept (ppm) Observed	r	n
1[a]	C-1	S_p	1.32	128.52	127.87	0.998	8
	C-2,6	S_m	1.05	134.39	134.37	0.854	8
	C-3,5	S_o	1.02	129.10	129.12	0.999	8
	C-4	S_i	0.97	129.64	129.35	0.999	8
2[a]	C-1	S_p	1.35	127.94	127.20	0.997	8
	C-2,6	S_m	1.07	134.97	134.97	0.893	8
	C-3,5	S_o	1.02	129.11	129.10	0.999	8
	C-4	S_i	0.97	129.71	129.40	0.999	8
3[a]	C-1	S_p	1.30	128.28	127.52	0.997	7
	C-2,6	S_m	1.17	134.46	134.50	0.873	7
	C-3,5	S_o	0.96	129.91	129.10	0.994	7
	C-4	S_i	0.98	128.79	129.32	0.998	7
DPS-I[b]	C-1	S_p	1.64	137.36	135.72	0.991	9
DPS-II[b]	C-1	S_p	1.52	131.70	130.33	0.994	7
DPS-III[b]	C-1	S_p	1.04	135.66	135.72	0.996	8
PVS[c]	C-1	S_p	1.54	—	—	—	—
PMS[d]	C-1	S_p	1.14	138.77	138.60	0.992	7

[a] This work.
[b] Ref. 10.
[c] Ref. 13.
[d] Ref. 14

The b and ρ_R values in Table 8 and the fair correlation between them ($r = 0.961$) with a slope of 0.94 support the conclusions of Bromilow *et al.*[16] The values of b obtained for Series 1–3 (Table 8) lie in the order:



DPS-I: Y=H
DPS-II: Y=NO_2
DPS-III: Y=X
PMS: Y = Me
PVS: Y = CH=CH_2

Table 8. Comparison of Lynch slope (b) and resonance transmission ratios for carbons *para* to the variable substituent [$\rho_R(Y)/\rho_R(H)$]

Y	b	$\rho_R(Y)/\rho_R(H)$[a]
$SCOCH_3$[b]	1.32	1.28
$SCOC_6H_5$[b]	1.34	1.30
$SCOCH{=}CHC_6H_5$[b]	1.28	1.25
SC_6H_5[c]	1.64	1.68
$SC_6H_4NO_2$-4′[c]	1.53	1.47
SC_6H_4X-4′[c]	1.04	1.03
$SCH{=}CH_2$[d]	1.54	1.38
SCH_3[e]	1.14	1.13

[a] $\rho_R(Y)$ and $\rho_R(H)$ are the resonance coefficients in DSP correlation [$\rho_R(H) = 21.5$].[15]
[b] This work.
[c] The ^{13}C SCS values given in Ref. 10 have been correlated using σ_I and σ_R^0 constants.
[d] From Ref. 13.
[e] From Ref. 14.

$SC_6H_5 = SCH = CH_2 = SC_6H_4NO_2$-4′ > $SCOCH_3 = SCOC_6H_5 = COCH = CHC_6H_5$ > $SCH_3 = SC_6H_4X$-4′. This shows that the amplification of substituent effects by the acylthio functionality lies in the middle of the above series.

The Lynch correlations of ^{13}C chemical shifts of C-2, 6 for all the series of phenylthio esters with appropriate SCS values (S_m) give only scattered plots, revealing that the fixed thiol ester function influences the chemical shifts at these positions significantly. The ^{13}C chemical shifts of C-3,5 and C-4 carbons afford almost unit slopes, suggesting the lack of a significant influence by the acylthio group at these positions.

Hammett and dual substituent parameter (DSP) correlations

The ^{13}C chemical shifts of C-1 and carbonyl carbon afford satisfactory correlations with σ_p^+ constants

Table 9. Results of Hammett correlations of C-1 and carbonyl carbon chemical shifts using σ_p^+ constants

Series	Atom	ρ	Intercept	r	n
1	C-1	9.04	126.66	0.965	8
	CO	−1.94	193.52	0.977	8
2	C-1	9.30	125.99	0.968	8
	CO	−1.57	189.62	0.971	8
3	C-1	11.18	126.13	0.955	7
	CO	−2.31	187.34	0.973	7

Table 10. Results of DSP correlations of chemical shifts of Series 1–3 with σ_1 and σ_R^0 constants

Series	Atom	ρ_I	ρ_R	R	λ	n	Range of δ (ppm)
1	C-1	7.10	27.48	0.999	3.87	8	23.62
	C-2,6	2.10	−3.15	0.940	−1.53	8	2.15
	CO	−2.81	−4.76	0.993	1.69	8	4.97
	$COCH_3$	0.37	0.85	0.993	2.28	8	0.80
2	C-1	7.52	28.01	0.999	3.72	8	24.23
	C-2,6	2.25	−2.97	0.941	−1.32	8	2.17
	CO	−2.27	−3.94	0.997	1.74	8	4.08
	C-1′	−1.30	−0.51	—[a]	0.39	8	2.42
	C-2′,6′	0.40	0.14	0.959	0.36	8	0.24
	C-3′,5′	0.24	0.15	0.921	0.63	8	0.39
	C-4′	0.84	0.69	0.986	0.82	8	1.00
3	C-1	7.14	27.03	0.999	3.79	7	18.17
	C-2,6	1.66	−3.87	0.973	−2.33	7	1.97
	CO	−2.97	−3.94	0.989	1.33	7	3.47
	C-α	−0.81	−0.44	0.989	0.55	7	0.66
	C-β	1.51	1.90	0.983	1.26	7	1.63
	C-1′	−0.50	−0.30	—[a]	0.68	7	0.47
	C-4′	0.56	0.62	—[a]	1.12	7	0.66

[a] Poor correlation.

(Table 9). The sign of the ρ values show 'normal' and 'inverse' substituent effects for C-1 and carbonyl carbons, respectively. DSP correlations of the chemical shifts of Series 1–3 afford several good correlations (Table 10). The magnitude of ρ_I and ρ_R values obtained for C-1 of Series 1–3 are greater than the magnitude of ρ_I and ρ_R values obtained for the monosubstituted benzenes, $\rho_I = 4.6$ and $\rho_R = 21.5$. This also reveals amplification of substituent effects at C-1 just as concluded from Lynch correlations. The C-2,6 carbons, in a *meta* relationship to the variable substituent X, correlate reasonably well with σ_I and σ_R°, affording negative ρ_R values (Table 10) and suggesting an inverse resonance effect. Similar negative ρ_R values for *meta* carbons have previously been observed for several series of 1,4-disubstituted benzenes.[15] The origin of the negative sign of ρ_R for the *meta* carbons is not clear.

The correlations of carbonyl carbon of Series 1–3 afford negative ρ_I and ρ_R values, suggesting inverse substituent effects. This could be taken as an evidence for π-polarization of the thiol ester functionality by the dipole of the substituent (**4**).

It is pertinent to note that such inverse substituent effects, suggesting π-polarization, have been reported for carbons of a few unsaturated side-chains attached to aromatic systems.[16] The data in Table 11 compare the ρ_I and ρ_R values of carbonyl carbons of Series 1–3 with that of carbonyl carbons of 4-substituted phenyl acetates[16] (Series 4) and 4-substituted *N*-arylacetamides[17] (Series 5). That the extent of π-polarization of the carbonyl group of all three series of thiol esters remains roughly equal is evident from almost equal ρ_I and ρ_R values (Table 11). The data in Table 11 also reveal an inverse substituent effect for the carbonyl carbon of the $OCOCH_3$ group but to a lesser extent. In contrast, the $NHCOCH_3$ group has positive ρ_I and ρ_R values, revealing a normal substituent effect. It appears that the large resonance interaction between the nitrogen and carbonyl in the amide group overshadows the π-polarization interaction, while the ester and also the thiol ester groups, with diminished resonance interaction between 'O'/'S' and carbonyl, display a significant π-polarization interaction. Inspection of

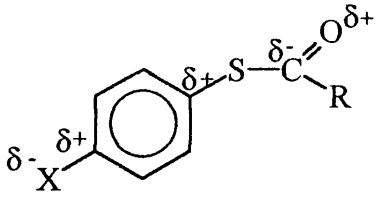


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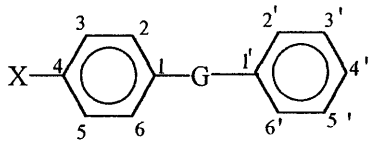
Table 11. Results of DSP analyses of carbonyl carbon chemical shifts

Series	ρ_I	ρ_R	λ	R	n
1[a]	−2.81	−4.76	1.69	0.993	8
2[a]	−2.27	−3.94	1.74	0.997	8
3[a]	−2.97	−3.94	1.33	0.989	7
4[b]	−1.21	−1.82	1.50	0.989	13
5[b]	0.96	2.58	2.68	0.991	11

[a] This work.
[b] The SCS values of 4-substituted phenyl acetates (Series 4) and 4-substituted *N*-arylacetamides (Series 5) have been taken from Refs 16 and 17, respectively.

the ρ_R values of unsubstituted phenyl ring of Series 2 (Table 12) reveals that C-1′ has a negative ρ_R value whereas C-2′,6′; C-3′,5′ and C-4′ have positive ρ_R values. This could be ascribed to the involvement of a localized π-polarization mechanism in this system, resulting in separate polarization of the carbonyl group and the unsubstituted phenyl ring in Series 2 by the dipole of the substituent. The low ρ_R values of C-2′,6′ and C-3′,5′ relative to C-4′ suggest that π-polarization is effective along the C-1′—C-4′ axis.

The negative sign of the ρ_R values of the carbonyl carbon, C-α and C-1′ and the positive sign of ρ_R values for C-β and C-4′ observed in Series 3 (Table 12) show that each discrete π-system in this series, viz. carbonyl group, —CH=CH— and the unsubstituted phenyl ring, suffers separate polarization (localized polarization). The data in Table 12 give ρ_I and ρ_R values for systems of the general form **5** in which a localized π-polarization mechanism is known to be involved. Although the extent of π-polarization in different series of the form **5** varies, as is evident from the variation in the ρ_R values of C-1′ and C-4′ (inverse effect for C-1′ and normal effect for C-4′), the trend of substituent effects is found to be the same.



G = -SCO-, SCOCH=CH-, -S-, -CO-, -COCH=CH-

5

^{17}O NMR study of 4-substituted phenylthiol acetates

^{17}O NMR spectra of a few 4-substituted phenylthiol acetates as a representative series were measured at 54.22 MHz. The ^{17}O chemical shifts for four compounds of Series 1 [X=N(CH$_3$)$_2$, 512.5; OCH$_3$, 513.6; H, 513.9; NO$_2$, 513.9 ppm] show that even substituents which differ in their electronic character to a large extent such as 4-nitro, 4-methoxy and 4-*N*,*N*-dimethylamino fail to influence the chemical shift of the oxygen of the thiol ester group significantly. The variation in these chemical shifts (1.4 ppm) is small, almost of the same order as the accuracy of ^{17}O chemical shifts (1.0 ppm). This observation suggests that the electron density on the oxygen atom of these thiol acetates remains almost constant, ruling out significant conjugative and π-polarization interactions between the sulphur atom and the carbonyl group. The π-polarization and conjugation are expected to cause 'normal' substituent effects on the ^{17}O chemical shifts of the carbonyl oxygen. This is in sharp contrast to the inference, from the inverse effect on the carbonyl carbon chemical shifts, that there are significant π-polarization interactions in all the series of thiol esters. The origin of the difference between the substituent effects on the carbonyl carbon and oxygen is unclear.

It is pertinent to note that ^{17}O chemical shifts of a series of substituted phenyl acetates also show insensitivity to steric effects.[19] This has been ascribed by Boykin *et al.*[19] to (i) the large torsion angles (calculated by MM2) and the relatively small changes in torsion angle predicted with increasing steric hindrance and (ii) the competition between two overlaps, one involving

Table 12. DSP analyses of ^{13}C SCS data for side-chain and unsubstituted phenyl group in 4-XC$_6$H$_4$—G—C$_6$H$_5$

G	Atom	ρ_I	ρ_R	Scale	R or (f)
—SCO—[a]	C-1′	−1.30	−0.51	σ_R° (NMR)	poor
	C-2′,6′	0.40	0.14	σ_R° (NMR)	0.959
	C-3′,5′	0.24	0.15	σ_R° (NMR)	0.921
	C-4′	0.84	0.69	σ_R° (NMR)	0.986
—SCOCH=CH—[a]	C-1′	−0.50	−0.34	σ_R° (NMR)	0.840
	C-4′	0.56	0.62	σ_R° (NMR)	0.899
	C-α	−0.81	−0.44	σ_R° (NMR)	0.989
	C-β	1.15	1.90	σ_R° (NMR)	0.983
—S—[b]	C-1′	−4.96	−11.7	σ_R° (NMR)	0.993
	C-4′	2.7	5.4	σ_R° (NMR)	0.997
—CO—[c]	C-1′	1.6	−1.9	σ_R°	(0.10)
	C-4′	1.3	2.0	σ_R°	(0.10)
—COCH=CH—[c]	C-1′	−0.8	−0.4	σ_R BA	(0.21)
	C-4′	0.3	0.6	σ_R°	(0.27)
	C-α	−1.1	−0.06	σ_R^+	(0.31)
	C-β	3.7	3.1	σ_R^+	(0.08)

[a] This work.
[b] Ref. 10.
[c] Ref. 18.

the oxygen lone pair containing orbitals and the orbital of the phenyl ring and the other involving the oxygen lone pair orbital and the orbital of the carbonyl carbon.

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