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Density functional theory calculations of ^{17}O and ^{13}C NMR chemical shifts for aromatic acyl chlorides

Ito Chao,[1]* Ko-Wen Chen,[2] Tsong-Song Hwang[1] and Kwang-Ting Liu[2]*

[1]Institute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan (ROC)
[2]Department of Chemistry, National Taiwan University, Taipei 106, Taiwan (ROC)

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epoc ABSTRACT: Density functional theory (DFT) at the B3LYP/6–31 + G(d,p)//B3LYP/6–31G(d) level was used to calculate ^{17}O and ^{13}C NMR chemical shifts of the carbonyl group of aromatic acyl chlorides **1a**–**n**. The aryl groups included substituted phenyl, furyl, thienyl and naphthyl. The calculated ^{17}O chemical shifts correlated well with the experimental values and with Hammett-type σ^+ constants. Therefore, in many cases it is possible to deduce σ^+ constants of substituted aryl groups via gas-phase calculation of ^{17}O chemical shifts of the carbonyl groups. The σ^+ values obtained in the gas-phase calculation show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of the environment. Furthermore, the concept of n–π* mixing can be used to understand the sensitivity of the O and Cl atoms and the insensitivity of the C atom towards substituent effects in aromatic acyl chlorides. Copyright © 2001 John Wiley & Sons, Ltd.
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KEYWORDS: ^{17}O chemical shift; theoretical calculation; substituent constant; n–π* mixing; solvolysis; solvent effect

INTRODUCTION

With the use of substituted acetophenones and benzaldehydes, it has been shown that the ^{17}O NMR chemical shift $\delta(^{17}\mathrm{O})$ of a carbonyl group is sensitive to substituents of the neighboring phenyl group.[1,2] Studies of acyl-containing compounds such as acids, amides, esters and other derivatives of carboxylic acids [YC(=O)X] have also confirmed the sensitivity of ^{17}O chemical shifts in reflecting the electronic nature of substituents X and Y.[3–9] Owing to this sensitivity, ^{17}O chemical shifts have been studied from different viewpoints. Dahn and coworkers used them to establish a scale of electrophilicity of the carbonyl group.[3–5] Others used them to study the effectiveness of transmission of the substituent effect.[9–13] It was found that an excellent linear correlation existed between σ^+ and ^{17}O chemical shifts measured in the nonpolar solvent CCl_4 for 12 α,α,α-trifluoroacetophenones (correlation coefficient $R = 0.998$).[7] Extending the study of benzene derivatives of trifluoroacetyl compounds to heteroaromatic derivatives such as furyl and thienyl, the same correlation between σ^+ and ^{17}O chemical shifts was also observed, except in the case of 3-furyl.[14] More recently, we demonstrated that density functional theory (DFT) calculations of ^{17}O chemical shifts at the B3LYP/6–31 + G(d,p)//B3LYP/6–31G(d) level of the above trifluoroacetyl compounds were compatible with the experimental values measured in CCl_4.[15] The small deviation (absolute values of <5 ppm in most cases) of the calculated values from the experimental values might be fortuitous, but the good correlation between the calculated and observed values is important. An excellent linear correlation ($R = 0.993$) between the calculated and observed ^{17}O chemical shifts of 15 trifluoroacetyl compounds was obtained when the data for the 3-furyl compound was excluded. Therefore, for functional groups the σ^+ values of which are difficult to deduce experimentally, theoretical calculation of ^{17}O chemical shifts of corresponding carbonyl compounds seems to be a potential substitute.

In contrast to the high sensitivity of the oxygen atom to the donor/acceptor ability of a neighboring group, the ^{13}C chemical shift of the carbonyl carbon atom is less dependent on the electronic nature of a neighboring group.[11,12,16,17] Analysis of components of shielding tensors of HCOX with *ab initio* calculation has revealed that n–π* mixing contributes to the sensitivity of ^{17}O chemical shifts toward the nature of X.[16] As the n-orbital is basically localized on the oxygen atom, the sensitivity observed on the oxygen atom does not occur on the carbon atom.

In order to establish whether the good correlations

**Correspondence to:* I. Chao, Institute of Chemistry, Academia Sinica, Nanking, Taipei 115, Taiwan (ROC). E-mail: ichao@chem.sinica.edu.tw or K.-T. Liu, Department of Chemistry, National Taiwan University, Taipei 106, Taiwan (ROC). E-mail: ktliu@ccms.ntu.edu.tw
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Table 1. Calculated and experimentally observed chemical shifts of aromatic acyl chlorides

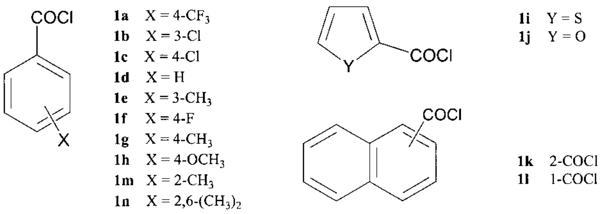
ArCOCl	Ar	σ^+	$\delta(^{17}O)_{calc}$	$\delta(^{17}O)_{obs,CCl_4}$	$\delta(^{17}O)_{obs,CH_3CN}$	$\Delta\delta_{CCl_4}$[a]	$\Delta\delta_{CH_3CN}$[b]	$\delta(^{13}C)_{calc}$	$\delta(^{13}C)_{obs}$	$\Delta\delta$[c]	$\sigma_{iso}(Cl)_{calc}$
1a	4-$CF_3C_6H_4$	0.612	506.9	505.2	497.5	1.7	9.4	169.9	167.9	2.0	523.6
1b	3-ClC_6H_4	0.399	501.3	499.2		2.1		169.5	167.4	2.1	525.8
1c	4-ClC_6H_4	0.114	495.6	494.6	487.7	1.0	7.9	169.0	167.0	2.0	532.1
1d	C_6H_5	0	494.8	493.6	485.5	1.2	9.3	170.1	168.0	2.1	531.5
1e	3-$CH_3C_6H_4$	−0.066	493.4	492.3		1.1		170.1	167.8	2.3	533.5
1f	4-FC_6H_4	−0.073	492.1	490.6	483.6	1.5	8.4	168.6	166.9	1.7	530.6
1g	4-$CH_3C_6H_4$	−0.311	489.2	487.7	479.3	1.5	9.9	169.3	167.6	1.7	534.2
1h	4-$CH_3OC_6H_4$	−0.778	479.4	477.4	468.9	2.0	10.5	168.2	165.3	2.9	540.4
1i	2-Thienyl	−0.928	479.5	476.7		2.8		160.2	159.3	0.9	511.3
1j	2-Furyl	−1.030	479.9	470.6		9.3		156.1	154.6	1.5	512.2
1k	2-Naphthyl	−0.126	493.7	489.0	485.3	4.7	8.4	170.1	172.2	−2.1	534.5
1l	1-Naphthyl		508.2	508.3	505.8	−0.1	2.4	169.3	175.2	−5.9	510.4
1m	2-$CH_3C_6H_4$		514.7	511.6	505.5	3.1	9.2	169.7	167.3	2.4	514.1
1n	2,6-$(CH_3)_2C_6H_3$		546.4	536.3	523.3	10.1	23.1	175.3	177.0	−1.7	423.8

[a] $\Delta\delta_{CCl_4} = \delta(^{17}O)_{calc} - \delta(^{17}O)_{obs,CCl_4}$.

[b] $\Delta\delta_{CH_3CN} = \delta(^{17}O)_{calc} - \delta(^{17}O)_{obs,\ CH_3CN}$.

[c] $\Delta\delta = \delta(^{13}C)_{calc} - \delta(^{13}C)_{obs}$.

between calculated and observed ^{17}O chemical shifts and between σ^+ constants and calculated ^{17}O chemical shifts also exist in systems other than the trifluoroacetyl compounds, we have studied other carbonyl compounds. In this paper, we present results for aromatic acyl chlorides (compounds **1a**–**n**). The aryl groups also include furyl, thienyl and naphthyl, not just limited to substituted phenyl of which the σ^+ constants vs observed ^{17}O chemical shift correlation have been reported in the literature.[8] In addition to the analysis of the ^{17}O chemical shifts of acyl chlorides, the ^{13}C chemical shifts of the acyl carbon atom were also analyzed to verify if the explanation deduced from the calculation of HCOX can be invoked to explain the sensitivity difference of ^{17}O and ^{13}C chemical shifts in ArCOCl.



1a X = 4-CF_3
1b X = 3-Cl
1c X = 4-Cl
1d X = H
1e X = 3-CH_3
1f X = 4-F
1g X = 4-CH_3
1h X = 4-OCH_3
1m X = 2-CH_3
1n X = 2,6-$(CH_3)_2$

1i Y = S
1j Y = O

1k 2-COCl
1l 1-COCl

EXPERIMENTAL AND COMPUTATIONAL DETAILS

^{17}O NMR spectra were recorded on a Bruker AM-300 WB spectrometer equipped with a 10 mm broadband probe operating at 40.670 MHz and values were reported relative to deuterium oxide. A 0.5 M solution in carbon tetrachloride was prepared in a dry-box. Perdeuterated benzene was used as the external lock. The recording temperature (51 °C) was corrected by using 80% ethylene glycol in DMSO-d_6 as the standard. A preliminary study of the unsubstituted benzoyl chloride indicated that 0.3 and 0.5 M solutions showed very close $\delta(^{17}O)$ values ($\Delta\delta = 0.3$ ppm). Therefore, 0.5 M is probably an appropriate concentration to minimize the possible dipole interactions between solute molecules. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer using chloroform-*d* solutions at ambient temperature (uncertainty: 0.5 ppm). The observed chemical shifts at natural abundance are given in Table 1.

Stable conformers of aromatic acyl chlorides were searched and checked with frequency analysis at the AM1 level.[18] The structures of the conformers found were further optimized and verified by frequency analysis at the B3LYP/6–31G(d) level. B3LYP means that Becke's three parameter functional[19a] is used for the exchange energy and the Lee, Yang and Parr functional[19b] for correlation energy. Single-point energy calculations and GIAO NMR chemical shift calculations[20] were carried out at the B3LYP/6–31 + G(d,p) level based on the B3LYP/6–31G(d) optimized structures. The energy differences at the B3LYP/6–31 + G(d,p) level between conformers were used to calculate the population of conformers according to the Boltzmann distribution ($T = 298$ K). The chemical shifts of conformers were all taken into account according to the population. All the semi-empirical calculations were carried out with the program SPARTAN 4.1.[21] The *ab initio* calculations were carried out with Gaussian 94,[22a] except for the orbital energies listed in the supplementary material, which were calculated with Gaussian 98.[22b]

To calculate the shielding tensor components (σ_{xx}, σ_{yy} and σ_{zz}), the convention of Dahn and Carrupt was followed.[23] In brief, the direction of the C=O bond is defined as the *z*-axis and the direction perpendicular to the acyl chloride plane is defined as the *x*-axis. Because the σ^+ constants for the *ortho*-substituted **1l**–**n** are not available, we only calculate the tensor components for **1a**–**k** in their lowest energy conformations.

RESULTS AND DISCUSSION

The calculated chemical shifts are analyzed in two directions. The degree of similarity between gas-phase calculated values and chemical shifts observed in non-polar CCl_4 is examined by plotting δ_{calc} against δ_{obs}. The sensitivity of the calculated chemical shifts to substituent effects in solvolysis reactions is checked by plotting δ_{calc} against σ^+. Table 1 shows the ^{17}O NMR chemical shifts of **1a**–**n**. The range of the ^{17}O NMR chemical shifts in CCl_4 is 470.6–536.3 ppm. The deviations between the calculated [$\delta(^{17}O)_{calc}$] and observed [$\delta(^{17}O)_{obs}$] chemical shifts are small (ca 2 ppm) for benzoyl chlorides **1a**–**h** and the calculated values are consistently downfield relative to the observed values. The $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation is excellent ($R = 0.999$) for **1a**–**h**. As the observed values correlate well with σ^+ constants ($R = 0.995$), the calculated values correlate equally well with σ^+ ($R = 0.996$). If *ortho*-substituted phenyl (**1m** and **n**), naphthyl (**1k** and **l**) and heteroaromatic (**1i** and **j**) acyl chlorides are all taken into account, the $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation (Fig. 1) is still reasonable ($R = 0.985$). Among the 14 compounds, the calculated chemical shifts of **1j** (2-furyl) and **1n** (2,6-dimethylphenyl) show the largest deviations (9–10 ppm) from the observed values. Basically, the magnitude of the deviations of $\delta(^{17}O)_{calc}$ from $\delta(^{17}O)_{obs}$ is similar to that in the trifluoroacetyl series.[15] For compounds without *ortho* substituents to the carbonyl group, **1a**–**k**, the correlation coefficient for the $\delta(^{17}O)_{calc}$–σ^+ correlation is 0.988 and for $\delta(^{17}O)_{obs}$–σ^+ it is 0.993. The reason for the large deviations for **1j** and **1n** is not clear. With two *ortho*-methyl groups, **1n** (2,6-dimethylphenyl) possesses the greatest steric congestion among the 14 acyl chlorides. The dihedral angle between the phenyl ring and the acyl plane is 58.5° in the calculated geometry of **1n** whereas the corresponding angle is no more than 5° in other

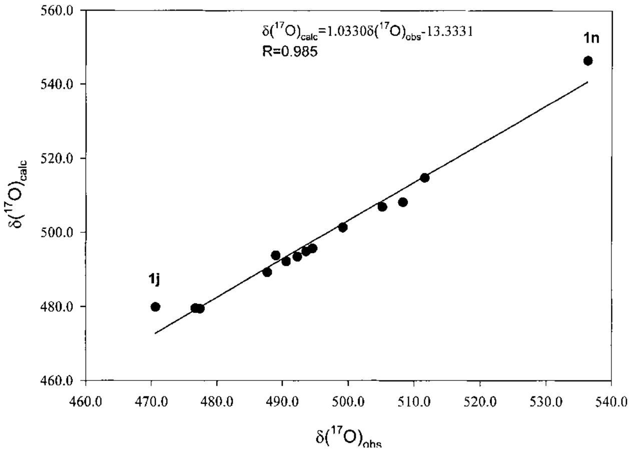


Figure 1. Correlation between $\delta(^{17}O)_{calc}$ and $\delta(^{17}O)_{obs}$ for compounds **1a–n**

compounds. Since proper treatment of electron correlation is important for NMR calculations as we have shown in Ref. 15 (p. 1002) that correlation between calculated and measured chemical shifts dropped if NMR calculations were carried out at the HF level, it is likely that better electron correlated theory levels are needed to handle sterically congestive systems such as **1n**.

In the literature, the ^{17}O chemical shifts measured in polar acetonitrile (CH_3CN) solvent[8,10] have been reported for **1a**, **c**, **d**, **f–h** and **k–n**. They were more upfield than that in the non-polar CCl_4 by several ppm in most cases (Table 1). The sterically congested **1n** has a larger deviation [$\delta(^{17}O)_{obs,CCl_4} - \delta(^{17}O)_{obs,CH_3CN} = 13$ ppm]. The correlation between gas-phase calculated chemical shifts [$\delta(^{17}O)_{calc}$] and those measured in CH_3CN [$\delta(^{17}O)_{obs,CH_3CN}$] is fair ($R = 0.968$). With the exclusion of **1n**, the correlation improves ($R = 0.985$). The corresponding R value for the $\delta(^{17}O)_{calc}$–$\delta(^{17}O)_{obs}$ correlation in CCl_4 with the same set of compounds (also excluding **1n**) is 0.992. The better correlation between calculated values and chemical shifts in the non-polar solvent demonstrate that gas-phase calculated chemical shifts are reasonable and they may be used as a control group to contrast the influence of solvents on solutes.

The ^{13}C chemical shifts of the carbonyl carbon atom of **1a–n** in $CDCl_3$ are in the range 154.6–177.0 ppm [Table 1, $\delta(^{13}C)_{obs}$]. Although the calculated chemical shifts deviate from the observed values by less than 5.9 ppm, the relatively small variation range of $\delta(^{13}C)_{obs}$ (ca 23 ppm) makes the $\delta(^{13}C)_{calc}$–$\delta(^{13}C)_{obs}$ correlation ($R = 0.904$) much worse than that for ^{17}O chemical shifts. Scattered $\delta(^{13}C)_{obs}$–σ^+ and $\delta(^{13}C)_{calc}$–σ^+ plots were obtained ($R < 0.77$) even if the sterically congested compounds **1l–n** were not included.

A chemical shift is the difference in isotropic shieldings [σ_{iso}; $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, where σ_{xx}, σ_{yy}, and σ_{zz} are the shielding tensor components in the x, y and z directions, respectively] between the reference compound and the measured compound. In the study of HCOX (X = SiH_3, H, Me, SH, Cl, F, OMe, OH, NH_2 and O^-), Dahn and Carrupt found that σ_{zz} of ^{17}O is far more sensitive than σ_{xx} and σ_{yy} to the electronic nature of X.[16] The range of σ_{zz} is -1649 (X = SiH_3) to -9 ppm (X = O^-), whereas the range of σ_{xx} is 414–215 ppm and that of σ_{yy} is -604 to -126 ppm. Shielding tensor component σ_{zz} is related to charge circulation in the x,y plane. Analyzing the mixing of unoccupied and occupied ground-state orbitals in the presence of a magnetic field from IGLO[24,25] calculation results, Dahn and Carrupt[16] found that the n (in the y direction)–π^* (in the x direction) mixing is the major cause of the large variation of σ_{zz} and is therefore responsible for the sensitivity of ^{17}O chemical shifts. On the other hand, the magnitudes of σ_{xx}, σ_{yy} and σ_{zz} of ^{13}C do not differ as much as in the case of ^{17}O. Furthermore, although some sensitivity towards X has been found for σ_{xx} and σ_{yy} of ^{13}C, the irregular variation of σ_{zz} results in a poor overall sensitivity of the carbonyl carbon atom towards X.[16] In brief, the ^{17}O shift values are strongly influenced by the n–π^* mixing, whereas the ^{13}C shift values are determined by multiple factors. The n–π^* mixing does not affect the ^{13}C chemical shifts because the lone pair is located on the O atom.

In comparison with HCOX, the ArCOCl system, with the presence of an aryl group, is more complex in terms of mixing of orbitals under the influence of a magnetic field. Whether a specific shielding tensor component still dominates the sensitivity of an atom is unclear. Using the same definition of the x, y, z, directions as in Dahn and Carrupt's study, we calculated σ_{xx}, σ_{yy} and σ_{zz} of carbonyl oxygen and carbon atoms and plotted them against σ^+ constants to examine whether the tensor components are sensitive to the substituent effect. As shown in Fig. 2, the slopes for σ_{xx}, σ_{yy} and σ_{zz} of ^{17}O are 6.68, -23.18 and -33.50, respectively; the correlation coefficients are 0.490, 0.992 and 0.920, respectively. Therefore, although σ_{zz} is inferior to σ_{yy} in correlating with σ^+, it is the most sensitive component toward substituent effects as judged by the slopes. This result is similar to that of HCOX in that σ_{yy} correlates the best with Hammett–Taft $\sigma_R{}^\circ$ constants, but is less sensitive than σ_{zz}.[16] Because the substituent effect is controlled by groups not directly bonded to the carbonyl group, unlike in the HCOX series, the variation ranges of the components are smaller in ArCOCl than in HCOX. When only the phenyl analogs **1a–h** ($\sigma^+ = 0.612$ to -0.188) are considered, all three components correlate well with σ^+ ($R = 0.988$, 0.997 and 0.996 for σ_{xx}, σ_{yy} and σ_{zz}, respectively). The slopes are 9.79, -24.25 and -42.30 for σ_{xx}, σ_{yy} and σ_{zz}, respectively, so σ_{zz} still contributes significantly to the variation of σ_{iso}.

Figure 3 shows the correlation between shielding tensor components of ^{13}C and σ^+ constants. All correlation coefficients are less satisfactory (<0.9) than those for ^{17}O. The slopes do not differ much from each

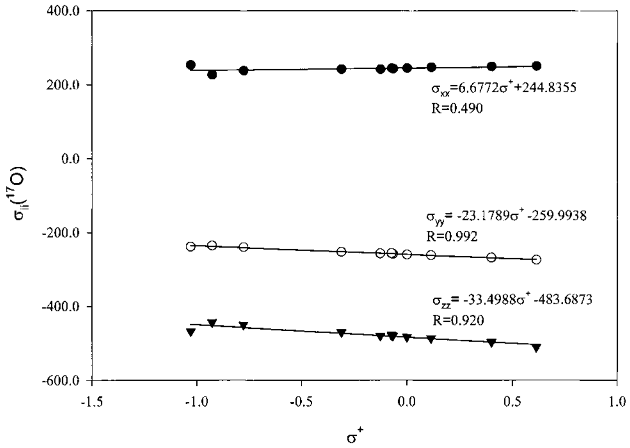


Figure 2. Plot of calculated σ_{ii} of ^{17}O against σ^+ constants for compounds **1a**–**k**

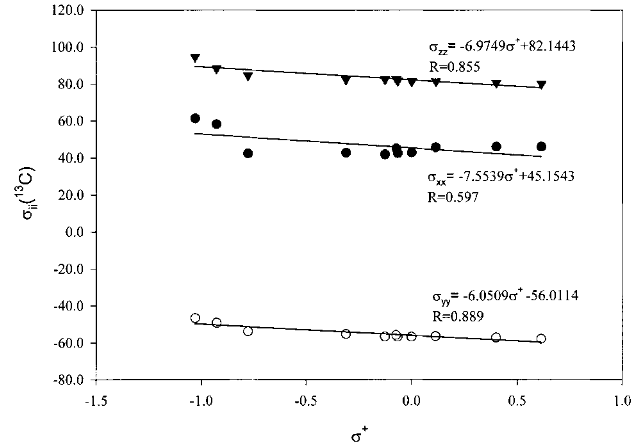


Figure 3. Plot of calculated σ_{ii} of ^{13}C against σ^+ constants for compounds **1a**–**k**

other, so the variation of σ_{iso} is not dominated by any specific component. Therefore, it will not be possible to describe the variation of ^{13}C chemical shifts qualitatively by a specific argument. Unlike for ^{17}O chemical shifts, the dominance of σ_{zz} makes the argument of n–π* mixing plausible.

Examination of frontier orbitals of the lowest energy conformer of **1a**–**h** shows that HOMO and HOMO-1 are π orbitals distributed basically on the phenyl ring. The HOMO-2 contains the oxygen lone pair along the *y*-axis (in the acyl chloride molecular plane and perpendicular to the C—O bond). The LUMO consists of π* of C—O and the phenyl ring. Therefore, the HOMO-2 to LUMO transition has the smallest energy gap among transitions that are responsible to the magnitude of $\sigma_{zz}(^{17}\mathrm{O})$. Plotting this n–$\pi$* energy gap against σ_{zz} and σ_{iso} of ^{17}O afforded a fair correlation (both $R \approx 0.96$) (only the lowest energy conformers of **1a**–**h** are used in finding the correlation; the values of orbital energies are reported in the supporting information at the epoc website at http://www.wiley.com/epoc). The HOMO–LUMO π–π* transition is irrelevant to the O atom, so it is not surprising that when the HOMO–LUMO gaps are plotted against σ (σ_{zz} or σ_{iso}), the correlation is very poor ($R < 0.4$).

Since HOMO-2 contains not only the lone pair of the oxygen atom, but also the lone pair of the chlorine atom in the *y,z* plane, we postulate that chlorine may also exhibit sensitivity towards substituent effects with a similar n–π* mixing mechanism. Plotting calculated σ_{zz} of the chlorine atom of sterically unhindered **1a**–**k** against σ^+ constants indeed shows a fair correlation ($R = 0.952$). Because the σ_{xx} of the two five-membered heteroaryl **1i** and **j** deviate significantly from the trend for other aromatic acyl chlorides (Fig. 4), it makes the σ_{iso} of these two compounds much smaller than one would expect on the basis of the σ^+ value (Table 1). To have a fair comparison between O, C and Cl, we use **1a**–**h** again to examine how well σ_{iso} of Cl reflects substituent effects. Plotting σ_{iso} of Cl against σ^+ gives a correlation coefficient of 0.972. This is worse than the $\delta(^{17}\mathrm{O})_{\mathrm{calc}}$–$\sigma^+$ correlation, but significantly better than the $\delta(^{13}\mathrm{C})_{\mathrm{calc}}$–$\sigma^+$ correlation.

CONCLUSION

We have shown that calculations of ^{17}O chemical shifts at the B3LYP/6–31 + G(d,p)//B3LYP/6–31G(d) level afford good results for ArCOCl, as found previously for ArCOCF$_3$. In general, the correlation between calculated and observed ^{17}O chemical shifts is good, especially when unhindered phenyl analogs are considered. Therefore, the calculation of ^{17}O chemical shifts has the potential to determine the σ^+ constant for a given group. It is known that σ^+ values (and also other substituent constants) for certain groups observed in different solvent systems are at significant variance.[26] The σ^+ values obtained in gas-phase calculations show the intrinsic

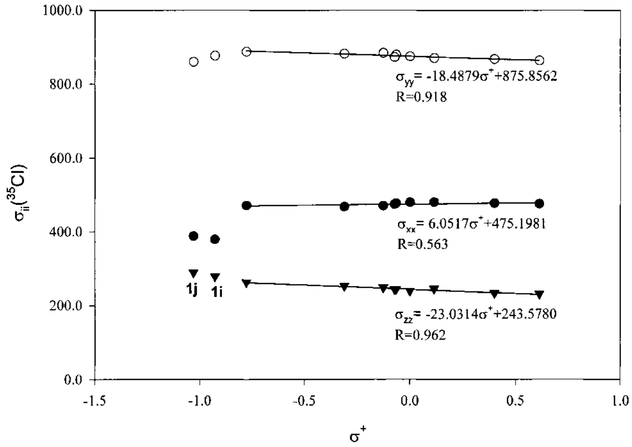


Figure 4. Plot of calculated σ_{ii} of Cl against σ^+ constants for compounds **1a**–**k**. The correlation is determined without the consideration of **1i** and **j**. When σ_{zz} of **1i** and **1j** are included in the $\sigma_{zz} - \sigma^+$ correlation, $R = 0.952$.

property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of the environment.

The calculated absolute deviation of ^{13}C chemical shifts from the observed values is similar to that for ^{17}O. Nevertheless, the significantly smaller variation range of observed ^{13}C chemical shifts of the carbonyl carbon atom makes the analysis of $\delta(^{13}\text{C})$ not worthwhile in terms of detecting substituent effects. Our results demonstrate that for ArCOCl the sensitivity of $\delta(^{17}\text{O})$ and the insensitivity of $\delta(^{13}\text{C})$ could be understood in terms of n–π^* mixing, in line with the conclusion obtained from HCOX by Dahn and co-workers. Furthermore, this concept leads us to analyze the σ_{iso} of Cl and we have found a correlation between σ_{iso}(Cl) and σ^+ for closely related compounds.

Supporting information

A table of calculated shielding tensors and a table of orbital energies of HOMO-2, HOMO and LUMO of lowest energy conformers of **1a**–**h** at the B3LYP/6–31 + G(d,p) level are available at the epoc website at http://www.wiley.com/epoc.

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