MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 589–592 (1997)

^{17}O NMR Spectra of Carbonyl Compounds ArCOX: Influence of Groups X on the Polarity of the Carbonyl Group†

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The ^{17}O shift values of *para*-substituted benzoyl compounds p-YC$_6$H$_4$COX (X = H, CF$_3$, COOEt, Br, Cl, F, SEt, OCOAr, OH, O$^-$Na$^+$, NH$_2$) were measured. The ^{17}O shielding values δ(^{17}O) of these and other aryl-unsubstituted benzoyl compounds (Y = H) follow the electron-donating power of X (resonance), whereas inductive electron attractors (CF$_3$, COOEt) show only small effects. The sensitivity of the shift values to donor/attractor *para* substituents Y, measured as the Hammett–Taft ρ$^+$ = δ(^{17}O)/σ$^+$, follows both the resonance and the inductive effects; combined with the δ(^{17}O) values, it is proposed as an empirical measure of the polarity (electrophilicity) of the carbonyl group (35 types of COX in Table 1).

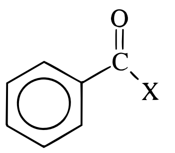
Magn. Reson. Chem. 35, 589–592 (1997) No. of Figures: 0 No. of Tables: 2 No. of References: 29

Keywords: NMR; ^{17}O NMR; carbonyl groups; resonance effects; aromatic substituent effects; benzoyl compounds; carbonyl group polarity

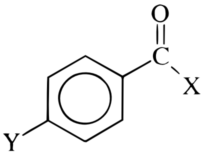
Received 7 February 1997; revised 14 March 1997; accepted 28 March 1997

INTRODUCTION

Several of the most important classes of organic compounds contain the carbonyl group as the essential function, e.g. aldehydes, ketones, carboxylic acids and their derivatives; the group is also present in metal carbonyl complexes. The chemical activity of the electrophilic carbonyl carbon varies widely; it is particularly diminished by electron-donating groups X in RCOX, e.g. esters, amides and carboxylate anions. It had been shown that the ^{17}O chemical shift values $\delta(^{17}\mathrm{O})$ follow qualitatively the electron-donating/attracting power of X.[2] This relationship exists empirically, although, in principle, chemical reactivity is not linked to the NMR shielding; the former is a property of the electronic ground state of the molecule, whereas the latter is a phenomenon in which excited states are mixed in to the ground states by the magnetic field. It is the purpose of this paper to complete the results of our preliminary communication[2] with the data for compounds of general structure **A** and **B**.



A



B

RESULTS AND DISCUSSION

In Table 1 we present the ^{17}O shift values of 35 benzoyl compounds PhCOX (without a substituent in the phenyl ring), part of which had already been published. Several of these compounds had also been measured in other laboratories;[3] for the sake of consistency, we remeasured them under identical conditions, particularly with respect to the solvent (MeCN, as far as possible).

As stated before,[4] the donor power of X, as conceived intuitively, plays a decisive role in determining the ^{17}O shift values in Table 1: when resonance increases the electron density around the oxygen atom, its shielding is strongly increased. A correlation between these values is, of course, not possible, as a scale of electrophilicity of —CO—X is lacking. [The Hammett–Taft substituent constants σ_{R^0},[5] assumed to represent the resonance donor capacity of X, do not give acceptable correlations with the $\delta(^{17}\mathrm{O})$ values for PhCOX.] While the shielding effect of donor groups X is clearly marked, the effect of acceptor groups X (CF$_3$, COOEt, CN), compared with standard groups such as H and Me, is practically absent. The deshielding effect of third-row (and higher) atoms such as Si has to be attributed to other reasons (see below).

However, the NMR shielding is not determined only by effects of electron density. On the basis of the Ramsay equation, the Karplus–Pople approximation has been developed:[6]

$$\sigma^{\mathrm{total}} = \sigma^{\mathrm{d}} + \sigma^{\mathrm{p}} \qquad (1)$$

$$\sigma^{\mathrm{p}} = -\mathrm{constant} \times \Delta E^{-1} \times r^{-3} \times \Sigma Q \qquad (2)$$

where σ_{p}, the essential structure-sensitive part of the total shielding, is determined by ΔE, the electronic exci-

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† NMR of Terminal Oxygen, Part 20. For Part 19, see Ref. 1.
Contract grant sponsor: Swiss National Science Foundation.

tation energy, r, the mean radius of the p-orbital at the atom measured and ΣQ, the charge density–bond order matrix. ΣQ contains the electron density mentioned above, mostly used by chemists to explain shift data, whereas ΔE^{-1} is active via the mixing-in by the magnetic field of unoccupied orbitals to the ground-state orbitals.

The importance of the ΔE^{-1} term manifests itself in many correlations between shift (or shielding) values and the UV–Vis maxima of (magnetically allowed) electronic transitions. In the case of carbonyl oxygen it has been shown that the n–π^* transition is the excitation essentially responsible for the strong deshielding of, e.g., formaldehyde; it is active by a magnetic moment in the direction of the C—O bond.[7] As the energy of the n–π^* transition increases with increasing resonance stabilization of the carbonyl group by electron donors (the UV maximum is displaced to shorter wavelengths), its deshielding action is diminishing, a factor as important for the ^{17}O shift as the increase of electron density.[1] The ^{13}C signal of the carbonyl carbon does not show this regular behaviour; thus the ^{13}C shift value is not at all useful for characterizing the electron deficiency at the carbonyl carbon. This is due to the fact that the n-orbital is essentially localized on O, which makes the n–π^* excitation inactive at C.[1]

Table 1. ^{17}O NMR chemical shifts $\delta(^{17}O)$ of PhCOX compounds and (*para*-) substituent sensitivities $\rho^+ [=\delta(^{17}O)/\sigma^+]$ of carbonyl compounds ArCOX

COX	δ^a	$\rho^{+\ a,b}$	n^c	Ref.
$COSiMe_3$	681.1	29.2	8	22
$COGeMe_3$	665.8	—		23
$COPPh_2$	608.9	24.2	6	22
$COPO(OMe)_2$	606.5	27.4	6	22
COTeBu	591.8	—		23
COI	571.0	—		23
CHO	562.1	26.3 (C)	9	—[d]
COCN	558.5	—		—[d]
COPh	552	—		3
COMe	548.6[e]	22.5	8	24
$COCH_2Br$	544.5	(20)	3	25
$COCH_2P^+Me_3$	543.8	(22)	3	25
$COCF_3$	543.6	29.0 (C)	10	—[d]
$COCH_2Cl$	542.2	—		25
COCOPh	543	26.6	7	26
COCOOEt	538.2	26.1	6	—[d]
COSeMe	525.2	—		23
$COCH_2SiMe_3$	524.4	—		25
COBr	513.3	23.8	7	—[d]
COSEt	489.5	16.0	8	—[d]
COCl	483.6	20.5 (C)	8	—[d,f]
CONCS	460.4	—		8
CONCO	451.5	(11)	3	8
CON=NCOAr	448.9	17.7	4	8
$COCHN_2$	439.9	9.9	8	25
CO-imidazolyl-1	430.8	(10)	2	8
CON_3	403.3	—		8
COOCOAr	386.4	13.2	9	—[d]
$COOPO(OMe)_2$	373.5	—		—[g]
COF	352.6	14.1	9	—[d]
COOMe	337.3	9.8	22	27
$COCH^-P^+Ph_3$	327.4	—		25
$CONH_2$	326.3	7.3	10	—[d]
COOH	246.1	7.3	7	—[d]
COO^-Na^+	265.3 (W)	5.1 (W)	12	—[d]

[a] Solvent MeCN, unless indicated otherwise; W = water depleted in ^{17}O; C = CCl_4.

[b] Substituent sensitivity $\rho^+ = \delta(^{17}O)/\sigma^+$; the values in parentheses are estimates.

[c] Number of data points for ρ^+.

[d] This work.

[e] Measured by Dr J. Zhuo.

[f] In MeCN: $\delta(^{17}O) = 485.5$ ppm; $\rho^+ = 21.2$ ($n = 9$); see Ref. 28.

[g] δ(COP) = 179.1 ppm, δ(PO) = 84.7 ppm (^1J = 171 Hz), δ(OMe) = 27.3 ppm; see also Ref. 29.

In silyl ketones $PhCOSiMe_3$ a strong Si–CO interaction manifests itself in a UV–Vis absorption at 424 nm and important deshielding [$\delta(^{17}O) = 681$ ppm]. It is probable that other third-row (and higher row) ligands, e.g. P, S and Cl, have analogous influences, although they are less easy to identify. In general, the maxima of the n–π^* transition, which is UV-forbidden, are not defined sharply enough to allow a good correlation of $\delta(^{17}O)$ with λ_{max}.

A special case is that of the benzoylazo compounds Ar—CO—N=N—CO—Ar, which, in spite of a long-wavelength UV–Vis absorption at 410–480 nm in a magnetically allowed n–π^* transition (ε = 40–60), are not less, but even more shielded [$\delta(^{17}O) \approx 450$ ppm] than aldehydes and ketones [$\delta(^{17}O) \approx 550$–$560$ ppm].[8] The reason for this deviation is that the n–π^* transition, responsible for the yellow colour, is located in the —N=N— group, which is only weakly conjugated with the carbonyl, so that its influence on the shielding of the carbonyl oxygen is strongly diminished. (Of course, this n–π^* transition localized on N is expected to be very active on the ^{15}N shielding, as in other azo compounds.[9])

Steric effects, which impose a torsion angle between the planes of the CO and the aryl groups and diminish the resonance between them, have been shown to increase the shift value $\delta(^{17}O)$; for instance, *o,o*′-disubstitution in PhCOOH causes a downfield shift $\Delta\delta(^{17}O) = +30$ ppm,[10] in PhCOOMe + 36 ppm,[10] in PhCOCl + 46 ppm[11] and in $PhCONH_2$ + 24 ppm;[10] in the absence of *o*-substituents, replacement of $CONH_2$ by the bulkier $CONMe_2$, which increases the torsion angle between the aromatic ring and the C=O plane, makes a downfield shift of + 22 ppm.[10] In the amides $PhCONH_2$ also, the carbonyl is not coplanar with the aryl ring; the possible effect of this torsion (see also below) on the δ value of $CONH_2$ can be roughly estimated by a comparison of the benzoyl with the corresponding non-hindered acetyl compounds:[3a] whereas in general (X = H, Me, Cl, F, OMe) the MeCOX compounds are *ca.* +20 ppm more deshielded than the corresponding PhCOX, the difference is −13 ppm for $CONH_2$, i.e. in the absence of torsion the δ value of benzamide might be *ca.* 30 ppm more shielded. This difference would not change the order of the $\delta(^{17}O)$ values in Table 1.

We compared the shift value of the strongly hindered *S*-ethyl 2,4,6-trimethylthiolbenzoate ArCOSEt (Table 2, footnote e) with that for the unhindered PhCOSEt, and found a deshielding effect $\Delta\delta(^{17}O) = +47$ ppm. This value is close to the analogous $\Delta\delta(^{17}O)$ for ArCOCl; as the latter group is coplanar in the absence of *o*-substituents (see below), we admit that the *o*-unsubstituted thiol ester also has no significant torsion angle. From models we conclude that the other groups COX in Table 2 (and most of those of Table 1) are in a similar situation as COSEt.

Substituent sensitivity

Another way to characterize the electrophilicity of the carbonyl group is based on the empirical principle that the effect of electron-attracting/donating substituents on the qualities of an electron-demanding centre is the greater, the more this centre is electron deficient. This 'tool of increasing electron demand',[12] successful in the past for determining the degree of unsaturation in carbocations,[13] has been applied to $\delta(^{17}O)$ of *para*-substituted benzoyl compounds;[2] in Table 2, the effect of substituents Y on the ^{17}O shifts of 11 new series of p-YC_6H_4COX compounds is shown; other series have been published before. It is evident from Table 2 that the range of $\delta(^{17}O)$ values between typical donor and acceptor substituents Y in YC_6H_4COX depends strongly on the character of X. To quantify the effect, the substituent sensitivity can be expressed, as usual, in terms of a Hammett-type relationship; in our case of electron-deficient benzoyl centres, the Hammett–Brown substituent constants σ^+ are appropriate;[5] they were conceived for the ArC^+Me_2 situation, but are often applied to $ArC^+(O^-)X$. For the compounds in Table 2 (and also for the others presented in Table 1), all groups COX gave statistically well behaved plots ($r \geqslant 0.98$) of $\rho^+ = \delta(^{17}O)/\sigma^+$.

The data in Table 1 show that, in general, the ρ^+ values parallel $\delta(^{17}O)$ of the unsubstituted compounds (Y = H). As expected, resonance-stabilized carbonyl groups, e.g. $CONH_2$ and COO^-Na^+, show a smaller substituent sensitivity ρ^+ than CHO. However, a plot of ρ^+ against $\delta(^{17}O)$ is statistically not good ($r \approx 0.93$); it could be improved by diminishing the influence of the ΔE^{-1} term, by dividing the δ values by the λ of the n–π* maximum. However, in contrast to the $\delta(^{17}O)$ values, the ρ^+ scale represents better the enhanced electron deficiency of electron-attractor groups, e.g. $COCF_3$ ($\rho^+ = 29$) compared with COMe ($\rho^+ = 22$).

Steric effects, which hinder coplanarity of the carbonyl group with the aromatic ring, are expected to diminish the influence of through-conjugation with the p-substituent Y, and thus diminish the value of ρ^+.[10] This has been shown, for the presence of hindering o,o'-substituents in the ring, by the difference between p-Y-acetophenones ($\rho^+ = 22$, Table 1) and 2,6-dimethyl-p-Y-acetophenones ($\rho^+ = 6$),[14] and, for the presence of a voluminous group X in COX in the absence of o-substituents, by the difference between p-Y-benzamides ($\rho^+ = 7.3$, Table 1) and N,N-dimethyl-p-Y-benzamides ($\rho^+ = 2.2$);[15] in the case of the amides, the presence of only one hindering group on N is not sufficient: N-methyl-p-Y-benzamides show $\rho^+ = 6.7$,[15] N-chloro-p-Y-benzamides $\rho^+ = 6.6$.[16] It has been demonstrated by different techniques that, in the absence of o,o'-substituents, most COX groups (CHO, COMe, COCl, COOH, COOMe) are coplanar (±2°) with the phenyl ring, whereas the $CONH_2$ group forms a torsion angle of *ca.* 30°.[10] Thus, among the compounds of Table 1, particularly the $CONH_2$ group can be suspected to exhibit a slightly too small ρ^+ value.[15,16] We do not think, however, that a correction for zero torsion for $PhCONH_2$ would seriously modify the general order of

Table 2. ^{17}**O NMR shifts values of carbonyl-O of** p-YC_6H_4COX **(solvent MeCN, unless indicated otherwise; *ca.* 40 °C)**[a]

						X					
Y	CF_3 [b]	H[b]	COOEt[c]	Br	Cl[b,d]	F	SEt[e]	OCOAr[f]	OH	NH_2	O^-Na^+ [g]
NMe_2	504.5	532.8				328.5	460.9	364.4		316.9	257.7
NH_2	506.0									315.6	258.9
OMe[h]	530.8	552.4	519.2	494.6	474.3	342.2	476.2	376.6	243.9	321.9	261.4
Me	544.6	565.7	531.7	506.1	485.4	348.8	484.3	382.0	246.1	324.1	263.2
t-Bu	546.5					349.2		386.1			
F	549.4	568.9				351.2		385.0	247.2	326.2	264.0
H	554.0	574.2	538.2	513.3	490.7	352.6	489.5	386.4	246.1	326.3	265.3
Cl	554.7	576.1	542.1	515.8	492.9	353.8	490.8		250.1	327.6	265.1
Br		577.5	542.9	516.4	493.0	354.4	490.9			328.4	265.7
I					493.7						265.4
CF_3	567.0							394.5	252.7		268.1
CN	567.4	593.6		529.8	504.3		498.3	394.3		332.9	269.5
NO_2 [i]		600.1	561.1	532.8	508.2	364.4	502.2	399.0	255.0	334.1	271.3

[a] Linewidths (in Hz): $X = CF_3$, 300–800; H, 120–280; COOEt, 270–900; Br, 90–240; Cl, 130–340; F, 70–140; SEt, 200–400; OCOAr, 330–900; OH, 60–140; NH_2, 100–180; O^-Na^+, 140–300.

[b] Solvent CCl_4.

[c] COOEt: $\delta(CO) = 354$–357 ppm, $\delta(—O—) = 167$–168 ppm.

[d] Further compound: Y = —N=S=O, $\delta(CO) = 497.6$, $\delta(NSO) = 428.5$ ppm.

[e] Further compounds: S-ethyl 2,4,6-trimethylthiolbenzoate, $\delta(^{17}O) = 536.5$ ppm (CCl_4); S-ethyl phenylthiolacetate, $PhCH_2COSEt$, $\delta(^{17}O) = 511.2$ ppm (CCl_4).

[f] $\delta(—O—)$ for $Y = NMe_2$, 237.9; OMe, 235.7; Me, 239.4; t-Bu, 241.1; H, 239.2; F, 238.7; CF_3, 240.1; CN, 243.4; NO_2, 241.0 ppm.

[g] Solvent H_2O.

[h] $\delta(OMe)$ for $X = CF_3$, 65.8; H, 61.4; COOEt, 66.2; Br, 68.4; Cl, 65.9; F, 66.5; SEt, 57.3; OCOAr, 64.1; OH, 58.5; NH_2, 55.1; O^-Na^+, 52.3 ppm.

[i] $\delta(NO_2)$ for X = H, 583.9; COOEt, 581.3; Br, 582.3; Cl, 586.5; F, 582.3; SEt, 584.3; OCOAr, 580.1; OH, 579.7; NH_2, 578.0 ppm.

ρ^+ values in Table 1; it would simply bring $CONH_2$ closer to COF and COOR. (The δ values of the COOH and COO^- groups are not comparable here, as the =O and —O— functions are averaged).

Three of the series in Table 2 were measured in solvents different from the standard MeCN; comparisons with literature data, and also some control comparisons that we measured, show, however, that the influence of the solvent on ρ^+ is not important (*ca.* ± 1 unit for CHO,[17] COMe,[17] $COCF_3$,[18] COCl,[11] COOH[19] and COOMe[19]). This contrasts with the important solvent sensitivity of $\delta(^{17}O)$[20] [with the exception of $COO - Na^+$, all $\delta(^{17}O)$ values in Table 1 (Y = H) were measured in MeCN].

CONCLUSION

In the absence of a better (and theoretically better founded) scale, we recommend the use of the $\rho^+ = \delta(^{17}O)/\sigma^+$ values as an indicator of the electrophilicity of —COX groups.

EXPERIMENTAL

Spectra

^{17}O NMR spectra were recorded on a Bruker WH-360 instrument equipped with a 10 mm probe at 48.8 MHz in the Fourier transform (FT) mode without lock. System control, data acquisitions and data management were performed by an Aspect-2000 microcomputer. The instrumental settings were as follows: spectral width 50 000 Hz (1025 ppm), 2K data points, pulse width 33 μs, acquisition time 20 ms, preacquisition delay 5 μs and 1.5K–2.3M scans; measurements were made with sample spinning (27 Hz). An even number (8–28) of left shifts (LS) were applied to the FID signal; the latter was zero-filled to 8K words, exponentially multiplied with a 100 Hz line-broadening factor (LB) before being subjected to FT. Chemical shifts are reported relative to $\delta(H_2O) = 0.00$ ppm; dioxane ($\delta = 0$ ppm) was used as an external standard; downfield shifts δ and increased shielding σ are positive. The reproducibility of chemical shift values was $< \pm 1$ ppm.

Compounds

Nearly all compounds measured were known, prepared by standard processes and characterized by m.p. determinations and ^1H NMR and IR spectra. Available commercial products (Fluka and Aldrich) were used without further purification. *S*-Ethyl 4-bromothiobenzoate, *p*-BrC_6H_4COSEt, prepared following Ref. 21, b.p. 150 °C/0.1 Torr (1 Torr = 133.3 Pa) (Kugelrohr), showed correct combustion analysis data; IR (film), 1660, 1580, 1480, 1390, 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz), 1.33 (t, $J = 7.8$ Hz, 3 H), 3.07 ppm (q, $J = 7.8$ Hz, 2 H), 7.55 (d, $J = 8.7$ Hz, 2 H), 7.80 (d, $J = 8.7$ Hz, 24).

Acknowledgement

This work was supported by the Swiss National Science Foundation. We thank Dr J. Zhuo for help with measurements and calculations.

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