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The Origin of the Difference Between the ^{13}C and ^{17}O Shift Behaviour of Carbonyl Compounds RCOX: *Ab initio* Calculation of the Shielding Tensors†

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In carbonyl compounds RCOX (X = H, Me, SiR_3, SR, Cl, F, OMe, OH, NH_2, O^-; R = H, Me), the ^{17}O shift values of the carbonyl group depend on the electron donor–acceptor properties of X, whereas the ^{13}C shift values are determined by other factors too. By IGLO *ab initio* calculations, the difference between ^{13}C and ^{17}O has been traced to differences in the relative importance of the shielding tensor component in the direction of the C—O bond (σ_{zz}). The deshielding contribution of this component is mainly determined by the energy of the n–π* excitation; donor–acceptor-type interactions influence the level of both orbitals. As the n orbital of this transition is essentially localized on the O atom, the excitation acts less on ^{13}C and is thus mainly responsible for the difference in substituent sensitivity between ^{13}C and ^{17}O shifts. An analogous difference of substituent sensitivities between ^{13}C and ^{17}O shifts exists in aroyl compounds *p*-YC_6H_4COX towards changes in the *para* substituent Y; it is explained on the same basis as the effect of X upon RCOX, without the necessity of referring to a 'reverse' substituent effect. Finally, the surprising absence of substituent effects upon the ^{17}O shift in aroyl cations *p*-$YC_6H_4CO^+$ can be explained by the fact that, for symmetry reasons, the n–π*-type excitation is absent in linear compounds. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Carbonyl groups, as in RCOX, are essential to several of the most important classes of organic compounds, such as aldehydes, ketones, acids and their derivatives. Their most general reaction is nucleophilic addition. Although the activity of the electrophilic carbonyl carbon varies widely and is particularly diminished by electron-donating groups X (as, e.g., in esters, amides and carboxylate anions), a generally accepted scale of electrophilicity of the carbonyl group is still lacking. We have observed that the ^{17}O chemical shift values, $\delta(^{17}O)$, of the carbonyl oxygen follow qualitatively the electron-donating or attracting power of X (although, in principle, reactivity, a property of the electronic ground state, is not linked to the chemical shifts, in which excited states are mixed in by the magnetic field; a better empirical correlation can be established by use of the substituent sensitivity of the shift value).[2] On the other hand, the ^{13}C shift values of the carbonyl carbon, $\delta(^{13}C)$, are much less dependent upon the character of X (Table 1):[3] the range of the $\delta(^{17}O)$ values is *ca.* 10 times larger than that of the $\delta(^{13}C)$ values, whereas the theoretical ratio is only 3.5 (see below). Furthermore, $\delta(^{13}C)$ varies with changes of X in a less systematic way than $\delta(^{17}O)$ and, in contrast to other cases of atoms linked

Table 1. ^{13}C and ^{17}O shift values of carbonyl groups in acetyl compounds MeCOX (ppm, from TMS and H_2O = zero, higher shielding negative)

Compound	δ(C)[a]	δ(O)[b]
$MeCOCF_3$	187	592[c]
MeCOH	200	592
MeCOMe	207	571
MeCOCl	170	502
MeCOF	161[d]	374[e]
MeCOOMe	171	361
$MeCONH_2$	173	313
MeCOOH	177	251

[a] Experimental data from Ref. 3.
[b] Experimental data from Ref. 46.
[c] Ref. 59.
[d] Ref. 15.
[e] Ref. 60.

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directly together, there is no good correlation between the two series of shift values. It was the purpose of this work to investigate the origin of this difference between ^{13}C and ^{17}O shifts in carbonyl compounds.

The shielding σ, which defines the chemical shift values δ, is not an isotropic property, but depends upon the orientation of the molecule in the magnetic field.[4] It can be described by a shielding tensor σ_{ii} with main components in the Cartesian axes i ($i = x, y, z$) (see below); for the same atom in a compound the components can differ by several hundred ppm, particularly in the case of π-systems. In regarding only the isotropic shielding value in solution σ_{iso}, which is the average of the three components, one loses valuable information. The important components of the shielding tensor, σ_{xx}, σ_{yy} and σ_{zz}, can be obtained by NMR measurements in the solid state or in liquid crystal solution, but also by other spectroscopic techniques.[4] For several simple carbonyl compounds RCOX the ^{13}C shielding tensor components have been measured by NMR techniques,[5] for instance MeCHO,[6,7] MeCOMe,[6] MeCOOH[6,8] and PhCOPh,[9] but also transition metal carbonyls.[10] For ^{17}O of carbonyl groups no tensor measurements of simple compounds RCOX seem to be available, with the exception of transition metal carbonyls.[10] Shielding tensor components can also reliably be obtained by *ab initio* calculations, e.g. IGLO.[11] Calculated ^{13}C shielding tensors of carbonyl compounds have been published, e.g., for CH_2O,[11–14] MeCHO,[14,15] HCOOH,[11,15] HCONHR[16] and HCOOMe,[11] but also for more complicated molecules like transition metal carbonyls[10] and DNA bases[17]. For ^{17}O, calculated shielding tensor components (semi-empirical and *ab initio*) have been published for CH_2O,[12,18] Me_2CO,[13] $HCONH_2$ and other amides,[13,19] DNA bases[17] and transition metal carbonyls[10] [although they must exist for other compounds also, for which only σ_{iso}(calc) has been published[11,20]]. Where available, the agreement between the calculated and experimental shielding tensor values is good.[10,11,15] For the purpose of comparison between the shielding tensors of different types of carbonyl compounds, we needed a homogeneous body of data; to obtain it, we (re)calculated by the IGLO program the shielding tensor components of a series of HCOX [X = SiH_3 (**1**), H (**2**), Me (**3**), SH (**4**), Cl (**5**), F (**6**), OMe (**7**), OH (**8**), NH_2 (**9**) and O^- (**10**)] compounds; we also performed calculations on several members of the series MeCOX (with the same X, except SiH_3, SH and OMe).

RESULTS

The results of our IGLO calculations of the shielding tensor components, σ_{ii}, for ^{13}C and ^{17}O of ten compounds HCOX (**1**–**10**) are presented in Tables 2 and 3, respectively. For a control, the calculated shift values δ(IGLO), obtained from the values of the isotropic shielding [$\sigma_{\mathrm{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, using[4] $\sigma(\mathrm{C}) = 185 - \delta(\mathrm{C})$ and $\sigma(\mathrm{O}) = 308 - \delta(\mathrm{O})$], are compared with the experimental shift values δ(exp) for HCOX or, if not available, for MeCOX (see below). In general, the difference between calculated and experimental shift values is small; we found for ^{13}C that δ(calc) is 10–20 ppm more shielded than δ(exp), 30 ppm in the case of the silyl ketone **1**. For ^{17}O, the difference is larger and in the opposite sense, i.e. δ(calc) is too deshielded; this had already been found for other calculations of $\delta(^{17}O)$ at the Hartree–Fock level,[11,20] neglecting electron correlation.[21] Another part of this difference can be attributed to solvent effects, which are particularly important for ^{17}O of the carbonyl oxygen;[22] indeed, the calculations refer to the gas phase whereas the measurements are made in slightly polar solvents. [The large difference between δ(IGLO) and δ(exp) for ^{17}O of HCOOH (**8**) is trivial; it stems from the fact that, in Table 3, we indicate the δ value of the C=O group, whereas the

Table 2. IGLO-calculated ^{13}C shielding tensor components σ_{xx}, σ_{yy} and σ_{zz} and shift values δ (calculated and experimental, ppm) for carbonyl carbon in HCOX

Compound	σ_{xx} [a]	σ_{yy} [a]	σ_{zz} [a]	σ_{iso} [a]	δ(IGLO)[b]	δ(exp)[b,c]
$HCOSiH_3$ (**1**)	124.3	−113.0	−109.6	−32.8	217.8	247.8[d]
HCOH (**2**)	123.0	−97.5	0.6	8.7	176.3	196.7[e]
HCOMe (**3**)	120.9	−101.0	−12.0	2.7	182.3	200.5
HCOSH (**4**)	111.8	−91.2	14.2	11.6	173.4	194.5[f]
HCOCl (**5**)	96.9	−87.2	92.6	34.1	150.9	170.4[g]
HCOF (**6**)	85.0	−80.9	131.1	45.1	139.9	161[h]
HCOOMe (**7**)	98.3	−74.0	77.5	33.9	151.1	160.9
HCOOH (**8**)	102.8	−76.1	80.5	35.8	149.2	166.4
$HCONH_2$ (**9**)	119.4	−69.0	56.0	35.5	149.5	167.6
$HCOO^-$ (**10**)	82.7	−43.0	49.6	29.8	155.2	182.6[i]

[a] $\sigma_{ii} = \sigma^{d}_{ii} + \sigma^{p}_{ii}$, absolute scale, $\sigma = 185 - \delta(^{13}C)$, higher shielding positive.
[b] δ: shift scale, relative to δ(TMS) = 0, higher shielding negative.
[c] Values from Ref. 3, solvent $CDCl_3$, unless indicated.
[d] $MeCOSiMe_3$, Ref. 61.
[e] Solvent dimethyl ether, Ref. 1.
[f] MeCOSH.
[g] MeCOCl.
[h] MeCOF.
[i] $MeCOO^-$, solvent H_2O.

Table 3. IGLO-calculated ^{17}O shielding tensor components σ_{xx}, σ_{yy} and σ_{zz} and shift values δ (calculated and experimental, ppm) for carbonyl oxygen in HCOX

Compound	σ_{xx}[a]	σ_{yy}[a]	σ_{zz}[a]	σ_{iso}[a]	δ(IGLO)[b]	δ(exp)[b,c]
$HCOSiH_3$ (**1**)	414	−604	−1649	−613	921	692[d]
HCOH (**2**)	410	−532	−1167	−429	737	648[e]
HCOMe (**3**)	364	−478	−951	−355	663	592[f]
HCOSH (**4**)	341	−413	−866	−313	621	511[g]
HCOCl (**5**)	305	−430	−739	−288	596	502[h]
HCOF (**6**)	289	−333	−300	−115	423	374[i]
HCOOMe (**7**)	331	−274	−322	−88	396	364[f]
HCOOH (**8**)	299	−279	−270	−83	391	(253)[f,j]
$HCONH_2$ (**9**)	352	−243	−312	−68	376	310[f]
$HCOO^-$ (**10**)	215	−126	−9	27	281	289[k]

[a] $\sigma_{ii} = \sigma^d_{ii} + \sigma^p_{ii}$, absolute scale, $\sigma(^{17}O) = 308 - \delta(^{17}O)$, higher shielding positive.
[b] δ: shift scale, relative to $\delta(^{17}O)(H_2O) = 0$, higher shielding negative.
[c] Values from Ref. 46, solvent MeCN, unless indicated.
[d] $MeCOSiMe_3$, Ref. 61.
[e] Ref. 1.
[f] Neat.
[g] MeCOSMe, Ref. 62.
[h] MeCOCl, neat.
[i] MeCOF, neat, Ref. 60.
[j] Mean value of δ(=O) and δ(—O—).
[k] Solvent water, Ref. 63.

spectrometer measures the average of δ(=O) and δ(—O—), as the proton is rapidly changing place between the two oxygens.]

For the shielding tensor components, the orientation of the molecular axes system (=molecular frame, MF) has been chosen as defined by convention:[23] the *x*-axis perpendicular to the molecular plane and the *z*-axis parallel to C—O (see Fig. 1). For reasons of comparison, we have maintained this orientation for all compounds **1**–**10** (see below).

It can be seen from Tables 2 and 3, and also from the plots in Figs 2 and 3 (for the abscissae in the latter, see below), that the shielding tensor component σ_{xx} is the direction of highest shielding for ^{13}C and for ^{17}O (with the exception of ^{13}C of HCOF, Table 2). This agrees with the general observation that in planar π-systems, olefins,[7,24] aromatic systems,[25] heteroaromatics,[26] carbonyl compounds,[5] imines,[27] etc., the direction of highest shielding for ^{13}C, ^{15}N and ^{17}O[28] is nearly always perpendicular to the molecular plane.[5,29] As, however, high shielding means a small (structure-characteristic) contribution to the isotropic chemical shift (= deshielding), this component is the least interesting.

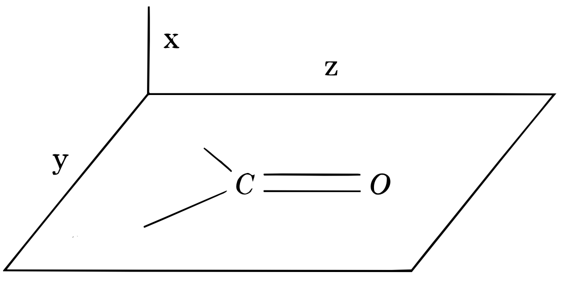

Figure 1. Molecular axes of HCOX.

The direction of the most important *de*shielding of ^{13}C is for all carbonyl compounds the *y*-axis (for **10**, see below). The same has been found for ^{13}C of olefins[24] and imines.[27] On the other hand, for ^{17}O of most of the carbonyl compounds examined here the *z*-axis is the most deshielded direction (Table 3), or close to it (for **10**, see below). The deshielding action of σ_{zz} is particularly important for compounds **1**–**5**, whereas for the compounds with more important donor groups X (**6**–**10**), the deshielding action of the component σ_{zz} diminishes to become more or less equal to that of σ_{yy} (Fig. 3).

For the purpose of our problem, the variability of σ_{xx}, σ_{yy} and σ_{zz} with variation of X is the most interesting aspect. It turns out (Tables 2 and 3) that for ^{13}C the range of values is narrow for σ_{xx}, *ca.* 40 ppm, whereas σ_{zz} is more affected (range *ca.* 240 ppm). For ^{17}O, σ_{xx} again varies least with variation of X (range *ca.* 200 ppm), whereas σ_{zz} is most sensitive (range >1600 ppm); (of course, the values for ^{13}C cannot be compared directly with those for ^{17}O). In other words, the shielding anisotropy, defined here as $\Delta\sigma = \sigma_{xx} - (\sigma_{yy} + \sigma_{zz})/2$, diminishes strongly with increasing donor power of X.

In Tables 2 and 3 we have presented the compounds HCOX **1**–**10** in the qualitative and intuitive order of increasing resonance-donating power of X (SiH_3 < H < Me < SH < Cl < F < OMe,OH < NH_2 < O^-). To evaluate the variation of the shielding tensor components σ_{ii} with the change of X, and for graphical presentations, we needed a numerical scale for the abscissa. As such we have chosen, somewhat arbitrarily, it is true, the Hammett–Taft σ_{R^0} function,[30] which is supposed to measure the groups' electron resonance effect; we use its numerical values as derived from IR and F NMR measurements.[30,31] We have to admit, however, that the

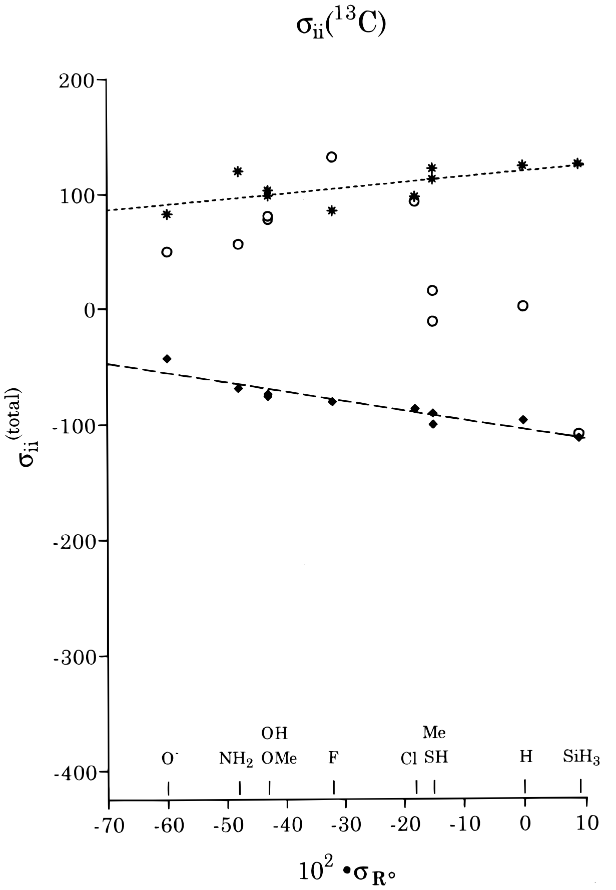

Figure 2. ^{13}C Shielding tensor components σ_{xx} (∗---∗), σ_{yy} (◆--◆) and σ_{zz} (○) (total shielding $\sigma = \sigma^{d} + \sigma^{p}$, in ppm, high shielding positive) of compounds HCOX (**1**–**9**) plotted against the Hammett–Taft constants σ_{R°(X) (see text).

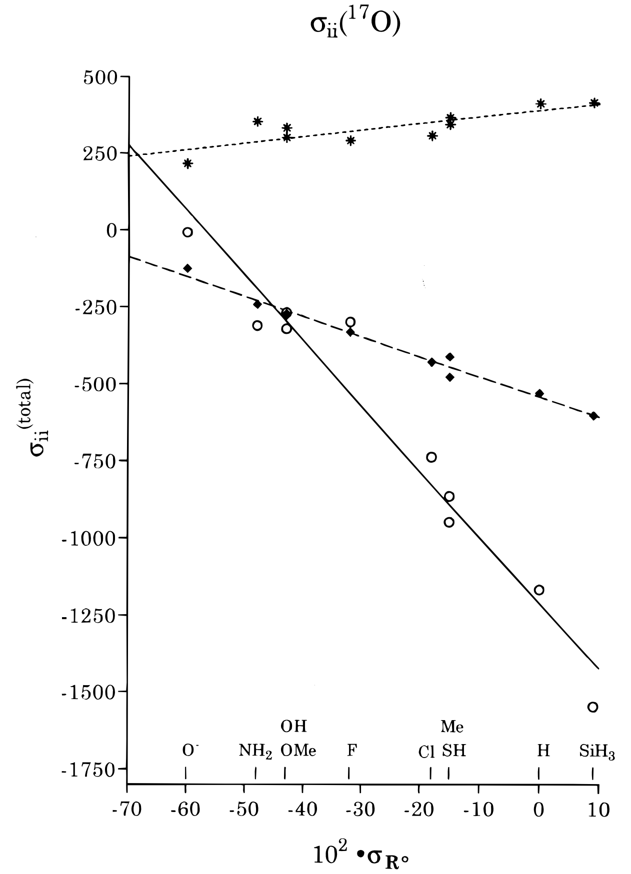

Figure 3. ^{17}O Shielding tensor components σ_{xx} (∗---∗), σ_{yy} (◆--◆) and σ_{zz} (○—○) (total shielding $\sigma = \sigma^{d} + \sigma^{p}$, in ppm, high shielding positive) of compounds HCOX (**1**–**9**), plotted against the Hammett–Taft constants σ_{R°(X) (see text). The scale of the ordinate is 1/3.5 times that in Fig. 2, corresponding to the theoretical ratio of ^{13}C to ^{17}O shielding, such that the slopes are visually directly comparable.

simple intuitive numerical order (**1**–**10**) in Tables 2 and 3, taken as abscissa values, gives 'correlations' which in both statistical quality and relative slopes yield the same picture as the substituent constant values of σ_{R°.

Plotting σ_{xx} against σ_{R°, we find for ^{13}C and ^{17}O only a slight dependence upon the donor character of X, with slopes $\sigma_{xx}(^{13}\mathrm{C})/\sigma_{R^\circ} = 46 \pm 12$ and $\sigma_{xx}(^{17}\mathrm{O})/\sigma_{R^\circ} = 210 \pm 38$; the values show a large scatter ($r = 0.66$ and 0.80, respectively), which can be attributed to the fact that the absolute (deshielding) activity of the components in the x direction is small, close to the error of the method. The dependence was better marked for the slopes $\sigma_{yy}(^{13}\mathrm{C})/\sigma_{R^\circ} = -83 \pm 7$ and $\sigma_{yy}(^{17}\mathrm{O})/\sigma_{R^\circ} = -650 \pm 21$ (with $r = 0.94$ and 0.990, respectively). The greatest difference between ^{13}C and ^{17}O is found in the shielding tensor component in the direction of the C—O bond (z-axis): for ^{17}O we find a (statistically reasonable) dependence upon the character of X, with a slope $\sigma_{zz}(^{17}\mathrm{O})/\sigma_{R^\circ} = -2200 \pm 135$ ($r = 0.97$), whereas for ^{13}C the scatter is so large that it is scarcely possible to draw a respectable straight line [$\sigma_{zz}(^{13}\mathrm{C})/\sigma_{R^\circ} \approx -210 \pm 53$ with $r = 0.68$]. Comparing the substituent sensitivities for ^{17}O and ^{13}C, one finds for the x direction the ratio of slopes $[\sigma_{xx}(^{17}\mathrm{O})/\sigma_{R^\circ}]/[\sigma_{xx}(^{13}\mathrm{C})/\sigma_{R^\circ}] \approx 4.6$, a value which deviates not very much from the theoretical value of 3.5 (the latter is due to the difference of the radii of the p-orbitals, see below[4,32]), leaving little place for a specific effect of X upon one of the atoms C and O. For σ_{yy} the ratio of the slopes $[\sigma_{yy}(^{17}\mathrm{O})/\sigma_{R^\circ}]/[\sigma_{yy}(^{13}\mathrm{C})/\sigma_{R^\circ}] = 7.8$ is significantly higher, pointing to a (slightly) greater influence of X upon O rather than C. For σ_{zz}, finally, as far as the large scatter in $\sigma_{zz}(^{13}\mathrm{C})$ allows an evaluation, the ratio of slopes $[\sigma_{zz}(^{17}\mathrm{O})/\sigma_{R^\circ}]/[\sigma_{zz}(^{13}\mathrm{C})/\sigma_{R^\circ}] \approx 10$ is about three times the theoretical $^{17}\mathrm{O}/^{13}\mathrm{C}$ ratio. In other words, the specific influence of X is particularly felt upon $\sigma_{zz}(^{17}\mathrm{O})$, i.e. in the direction of the C—O bond. This result will have to be discussed in terms of a qualitative MO picture.

The case of 10 and the effect of axes rotation

The actual values of the shielding tensor components σ_{yy} and σ_{zz} are sensitive to rotation of the axis system in the molecular plane, i.e. around the x-axis. It has been shown by measurements[33] and also by calculation[14] that for ^{13}C of non-symmetrical carbonyl compounds the directions of maximal deshielding ($\sigma_{11} < \sigma_{22}$, 'principal axes system,' PAS) do not coincide exactly with the molecular axes (y, z; MF system). The deviation is negligible (a few degrees) for aldehydes, ketones and esters;[33] it is 6–12° for amides,[34] and important only for carboxylate anions; here σ_{11} of ^{13}C is no longer in the y-direction but, for symmetry reasons (**10** is again a

C_{2v} molecule) turned by *ca.* 30° into the direction of the bisector of the O—C—O angle.[33] For ^{17}O, however, the deviation (found by IGLO calculation) is only a few degrees.[35] If one calculates for the anion HCOO$^-$ **10** the ^{13}C component in the C—O direction (σ_{zz}), the value of the deshielding is smaller than in the PAS system (σ_{22} in the direction of the O—C—O bisector). However, for the purpose of comparison of the shielding tensors of the carbonyl groups in different HCOX, we had to choose the MF, i.e. σ_{zz} always in the direction of the C—O bond.

One has to ask, however, whether the increase of shielding of ^{13}C and ^{17}O in HCOX in going from X = H to X = O$^-$ is not simply an artefact due to the simultaneous increase of the angle between the two axes systems MF and PAS. There are two arguments which show that this is not the case: (1) rotation of the RCOX plane around the *x*-axis, i.e. over the *y*, *z* coordinates, changes each of the tensor components σ_{yy} and σ_{zz} very considerably, but must necessarily leave the sum $\sigma_{yy} + \sigma_{zz}$ unchanged. [This is because the value of the isotropic shielding $\sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ is, of course, independent of the orientation, and on the other hand σ_{xx} cannot change upon rotation around the *x*-axis.] Actually, however, Tables 2 and 3 show that, on going from **1** to **10**, the sum $\sigma_{yy} + \sigma_{zz}$ changes considerably, leaving room for a genuine substituent effect. (2) From calculations[14,36] and also from measurements[33] of σ_{ii} as a function of rotation of the axes system one can evaluate that even an angle of 30° between σ_{zz} (MF) and σ_{22} (PAS; this is the extreme case for the ^{13}C shielding tensor in HCOO$^-$) implies a decrease of ≤ 30 ppm in $\sigma_{yy,\,zz}(^{13}\text{C})$ and ≤ 80 ppm in $\sigma_{yy,\,zz}(^{17}\text{O})$, i.e. very inferior to the effect actually observed in going from **1** to **10** (Tables 2 and 3).

MeCOX

We also calculated the shielding tensor components σ_{ii} and the isotropic shift values δ(calc) for ^{13}C and ^{17}O in MeCOX for most of the X in Tables 2 and 3. This was done because for several RCOX experimental values are available only for R = Me, not for R = H. It turned out that the difference in shift values δ(calc) between the two series is generally ≤ 20 ppm for ^{13}C, with $\delta(\text{R = Me}) > \delta(\text{R = H})$; for ^{17}O we found $\delta(\text{R = H}) > \delta(\text{R = Me})$, the difference sometimes being larger than for ^{13}C. These differences are, however, not far from the general uncertainty of our results; in the comparison of δ(calc) with δ(exp) in Tables 2 and 3, replacement of HCOX by MeCOX would even slightly improve the correlations. For convenience we will discuss here only the case of HCOX.

DISCUSSION

The total nuclear shielding σ is divided into a (shielding) diamagnetic σ^{d} and a (nearly always deshielding) paramagnetic part σ^{p}:[4]

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

The diamagnetic term σ^{d} depends only upon properties of the electronic ground state; σ^{d} is only slightly sensitive to variations of the molecular structure and can often be approximated by the (theoretical) value for the isolated atom,[37] which is $\sigma^{\text{d}}(\text{atom})(^{13}\text{C}) = 261$ ppm and $\sigma^{\text{d}}(\text{atom})(^{17}\text{O}) = 395$ ppm.[38] The IGLO procedure furnishes nearly constant contributions of σ^{d};[11] we found for compounds **1–10** values of $\sigma^{\text{d}}(^{13}\text{C})$ between 245 and 250 ppm and for $\sigma^{\text{d}}(^{17}\text{O})$ between 383 and 387 ppm (not shown in the tables), close to σ^{d}(atom). As a consequence of this low variability of σ^{d}, plots of σ^{p}_{ii} against $\boldsymbol{\sigma}_{\text{R}^0}$ are similar to those of the total shielding σ_{ii} against $\boldsymbol{\sigma}_{\text{R}^0}$ given in Figs 2 and 3 (although, of course, with different scales of the ordinate).

The paramagnetic term σ^{p} is that mainly responsible for the structure variability of the shielding and the shift values δ. The term σ^{p} is described by the quantum mechanical Ramsay equation,[4] which forms also the basis of *ab initio* calculations; in its form simplified by Karplus and Pople:[39]

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

it comprises three (not entirely independent) factors: (1) ΔE^{-1}, the inverse of the (average) electronic excitation energy; (2) r^{-3}, (the average of) the inverse cube of the radius of the 2p orbital on the atom measured; and (3) ΣQ, the bond order–charge density term. The last term, in its form of electron density, is the one mostly considered by chemists in qualitative discussions of chemical shifts. The radius term r^{-3} has been shown to be hardly sensitive to changes of molecular structure; it is, however, sensitive to changes of the atomic species: the increase in shift values by the factor 3.5 on going from ^{13}C to ^{17}O in analogous positions (see above) is generally attributed to this effect. Finally, the ΔE^{-1} term manifests itself in numerous correlations between shielding (or chemical shifts) and maxima in the UV–visible spectra, particularly long-wavelength absorptions.

Equations (1) and (2) are, of course, also valid for the individual components of the shielding tensor σ_{ii} $(= \sigma^{\text{d}}_{ii} + \sigma^{\text{p}}_{ii})$. In calculating σ^{p}_{ii} for compounds **1–10**, we find that for ^{13}C the deshielding is furnished by the three components in the ratio of *ca.* 20% σ^{p}_{xx}, *ca.* 50% σ^{p}_{yy} and *ca.* 30% of σ^{p}_{zz}, the ratio depending very little upon the structure of HCOX. For ^{17}O, this ratio is (for **2**) *ca.* $<1\%$ σ^{p}_{xx}, *ca.* 35% σ^{p}_{yy} and *ca.* 65% σ^{p}_{zz}, with the latter significantly decreasing from **1** to **5**.

In the following qualitative discussion we want to stress the importance of the electronic excitation term ΔE^{-1} for the interpretation of the shielding characteristics of ^{13}C and ^{17}O of carbonyl groups, but we will replace the average excitation energy of the approximation Eqn (2) by individual excitation terms. Of course the charge density–bond order term (ΣQ term) is also present: with increasing donating power of X (on going from **1** to **10**), the charge density around the O atom increases as the C=O bond order decreases; the accompanying changes in the ΣQ term at the C atom are less evident, as shown implicitly by Table 1. In particular, we want to demonstrate that the difference

Table 4. Principal orbital paramagnetic contributions σ^p (in ppm, higher shielding positive) to the components of the ^{13}C shielding tensor in HCOX

							X				
Component	Occ. orb.[a]	Virt. orb[b]	SiH_3	H	Me	SH	Cl	F	OMe	OH	NH_2
xx	σ_{CO}	σ^*_{CH}	−58.5	−61.9	−60.8	−73.0	−84.7	−87.0	−73.6	−73.5	−67.1
	π_{CO}		−0.4	−0.2	−0.4	−0.4	−0.3	−0.2	−0.1	−0.3	−0.4
	$\sigma_{CH,\,CX}$ [c]	σ^*_{CO}	−53.9	−54.5	−55.8	−50.7	−54.6	−65.7	−62.6	−60.9	−52.3
	LPO[d]		−3.7	−3.3	−1.3	−0.8	−1.4	−0.9	−0.1	0.6	−1.4
	$\Sigma\sigma^p_{xx}$		−118.5	−119.9	−120.4	−128.4	−142.3	−152.8	−139.7	−135.9	−122.0
yy	σ_{CO}	π^*	−227.4	−223.5	−223.2	−214.8	−212.9	−212.9	−207.5	−209.3	−201.8
	π_{CO}	σ^*	−42.0	−40.5	−37.7	−33.4	−35.7	−37.7	−32.7	−33.2	−29.2
	$\sigma_{CH,\,CX}$ [c]	π^*	−79.1	−70.1	−76.2	−77.5	−74.6	−71.5	−77.1	−75.2	−76.0
	LPO (n′)[d]	π^*	−19.7	−18.7	−19.0	−16.4	−19.0	−16.4	−15.4	−15.5	−15.0
	$\Sigma\sigma^p_{yy}$		−373.6	−352.5	−360.8	−351.3	−346.5	−337.7	−335.5	−334.7	−327.8
zz	σ_{CO}		0.1	−0.1	−0.1	0.4	0.6	−0.5	−0.3	−0.3	−0.2
	π_{CO}		27.5	24.8	23.4	36.1	35.6	16.1	16.5	17.0	20.1
	$\sigma_{CH,\,CX}$ [c]	π^*	−469.3	−353.8	−351.3	−327.4	−263.3	−189.7	−228.5	−228.1	−253.9
	LPO (n)[d]		77.5	67.4	62.7	76.3	80.8	56.0	47.8	47.0	45.4
	$\Sigma\sigma^p_{zz}$		−376.2	−261.8	−227.7	−251.0	−171.4	−131.2	−186.1	−182.7	−208.9
	σ^p_{iso} [e]		−289.4	−244.7	−253.0	−243.6	−220.1	−207.3	−220.4	−217.8	−219.5

[a] Occupied orbital.
[b] Virtual orbital (supposed).
[c] Sum of σ_{CH} and σ_{CX}.
[d] Lone pair orbitals.
[e] $\sigma^p_{iso} = (\sigma^p_{xx} + \sigma^p_{yy} + \sigma^p_{zz})/3$.

between C and O in the influence of the substituent X upon the paramagnetic part of the shielding can be explained on the basis of excitation energies.

In the NMR experiment, the magnetic field mixes an unoccupied (virtual) orbital into an occupied ground-state orbital. In order to be magnetically active, the corresponding electronic excitation has to involve a circulation of charge; the resulting magnetic vector is orthogonal to the plane of the charge circulation.[4] For instance, in the case of the carbonyl group, the longest wavelength UV absorption is that of the n–π^* excitation. The two n orbitals on oxygen, frequently considered as hybridized and symmetrical, can be localized as one n orbital with a lobe in the direction of the *y*-axis (often represented in a simplified way as the unchanged p_y orbital on oxygen), and another (n′) orbital with the lobe in the *z* direction (formed and stabilized by hybridization of the p_z orbital of the O atom with σ_{CO});[40] the π^* orbital presents lobes in the direction of the *x*-axis. An n–π^* transition thus involves a charge circulation in the *x*,*y* plane; consequently, the resulting magnetic vector is parallel to the *z*-axis.[9] Therefore, to deploy the full deshielding activity of the n–π^* transition in the NMR spectrum, the molecule has to be oriented with the C—O bond aligned with the external magnetic field; this is, of course, σ^p_{zz}, the paramagnetic part of the σ_{zz} component discussed above; the n–π^* transition cannot act magnetically in the direction of any of the other two Cartesian axes. Other contributions to the σ^p_{zz} deshielding component could come from other transitions equally involving charge rotation in the *x*,*y* plane (in the case of the C_{2v} molecule formaldehyde: symmetry type $b_1 \leftrightarrow b_2$); as they must necessarily be higher in energy than the HOMO–LUMO excitation n–π^*, their contribution to the deshielding must be weaker. Of the other excitations of the carbonyl group, the π–π^* transition, most prominent in the UV spectra, does not imply circulation, but only dipolar displacement of charge, and is thus magnetically inactive. For creating the deshielding part σ^p_{yy} of the σ_{yy} component of carbonyl compounds, it needs charge circulation in the *x*,*z* plane (for CH_2O: symmetry type $a_1 \leftrightarrow b_1$), which is brought about, e.g., by the n′–π^*_{CO} and the σ_{CO}–π^*_{CO} excitations, but also by π_{CO}–σ^*_{CO}, which belongs to the same symmetry type. Finally, the deshielding tensor component σ^p_{xx}, the weakest of the three, is created by charge circulation(s) in the *y*,*z* plane (formaldehyde: symmetry type $a_1 \leftrightarrow b_2$), e.g. n–σ^*_{CO},[12] as the transitions which are magnetically active in the *x* direction are high in energy (corresponding to absorptions in the far-UV region), they make, as observed, σ^p_{xx} the least deshielding component of the shielding tensor of formaldehyde, particularly for ^{17}O, but also for ^{13}C.

The IGLO procedure utilizes localized orbitals (LMO) to calculate the shielding; the program presents the results in terms of contributions of the LMO of the ground states, from which the excitations occur, rather than in terms of the excitations themselves, as given above (although, of course, the excitations are included in the IGLO procedure). As a consequence, the contributions of all excitations starting from the same ground-state LMO and presenting the same symmetry are added. However, as in most cases the energies of different excitations starting from the same ground state are different, we admit that, for a given ground state, the lowest energy excitation gives the main contribution of the LMO. This applies particularly to the most important deshielding contributions, those forming the σ^p_{yy} and σ^p_{zz} components. In our case, only for the deshielding contributions to the σ^p_{xx} component, several higher energy excitations are probable and might add; however, as this component contributes little to the total deshielding, it can be neglected in a first approximation. Thus we combine the directions of the magnetic moment of the required tensor component and that of the ground state orbital (both furnished by the calculation) with a guess of the probable (lowest energy) virtual orbital of the symmetry character requested to identify, at least qualitatively, the excitation most important for the contribution to a deshielding component. This procedure is confirmed by a comparison with the results of a careful older quantum chemical analysis of the tensor components of formaldehyde (**2**) by perturbed HF calculations,[12,41] which yielded the deshielding contributions of each individual excitation; for most of the deshielding contributions, the results of the HF calculations are in satisfactory agreement with the IGLO results (see below). The principal localized orbitals used by the IGLO calculations as ground states of various excitations are: (1) the lone pair orbitals on oxygen (LPO), i.e. as mentioned above, the higher energy n with the lobe in the y direction, and the stabilized n′ with a lobe in the z direction; (2) the π_{CO} orbital (direction: x); (3) the CH and CX σ bond orbitals (directions: y and z; in Tables 4 and 5, $\sigma_{CH,\,CX}$ represents the sum of these two); and (4) the σ_{CO} orbital (direction: z). In this enumeration, we have given the direction of the main lobes of the orbitals, instead of the correct symmetry symbols, because the latter change between the C_{2v} molecule **2** and the molecules **1** and **3**–**9** of C_s symmetry.

Tables 4 and 5 present the results of the IGLO calculations of ^{13}C and ^{17}O, respectively, for compounds **1**–**9** (**10** was not included owing to the change of the orientation of the axes system mentioned above; possibly the increased resonance and the negative charge also play a role). We shall discuss first the results for CH_2O (**2**), then the comparison with other compounds HCOX.

Formaldehyde

This compound has already been the object of calculations by the IGLO procedure, as well as other methods (HF-MO), yielding the tensor components and the LMO contributions.[11,12,18] For ^{17}O of **2**, the largest deshielding is in the σ^{p}_{zz} component; 88% of it is furnished by one of the LPO orbitals (Table 5). The LPO occupied orbital used must be n, the one possessing a lobe oriented in the y direction (symmetry b_2 for CH_2O), for the n′ orbital in the z direction cannot furnish a magnetic vector in the z direction. For a charge circulation in the x,y plane, necessary to create a magnetic moment in the z direction, the virtual orbital has to have a lobe oriented in the x direction; of those available for this direction, the π^* orbital has the lowest energy; no other low-lying unoccupied orbital is available. Hence it is reasonable to admit that the LPO contribution comes essentially from the n–π^*_{CO} transition [the earlier HF treatment[12] attributed 99% of the deshielding $\sigma^{p}_{zz}(^{17}O)$ component to the n–π^* excitation]. Lesser contributions to the $\sigma^{p}_{zz}(^{17}O)$ deshielding come from (1) the σ_{CH} occupied orbital (symmetry for CH_2O: b_2, orientation y), for which the x-oriented π^*_{CO} is the lowest energy unoccupied orbital available (excitation σ_{CH}–π^*_{CO}) and (2) the π_{CO} occupied orbital (symmetry for CH_2O: b_1, orientation x), which suggests the excitation π_{CO}–σ^*_{CH}. For the deshielding σ^{p}_{yy} component of ^{17}O of **2**, necessitating a charge rotation in the x,z plane, σ_{CO}, the major contributing ground-state orbital (contribution 56%), can be considered to act through the σ_{CO}–π^*_{CO} excitation. Of the two lesser contributors, π_{CO} can act through the π_{CO}–σ^*_{CO} excitation, and LPO, more particularly the lower energy n′ orbital (direction: z), via the n′–π^*_{CO} excitation. It seems surprising that σ_{CO} should

Table 5. Principal orbital paramagnetic contributions σ^{p} (in ppm, higher shielding positive) to the components of the ^{17}O shielding tensor in HCOX

Component	Occ. orb.[a]	Virt. orb[b]	X								
			SiH_3	H	Me	SH	Cl	F	OMe	OH	NH_2
xx	σ_{CO}		12.0	8.2	−2.3	−11.3	−25.2	−33.4	−17.3	−26.6	−11.5
	π_{CO}		0.2	0.2	0.3	0.2	0.2	0.1	0.0	0.1	0.1
	$\sigma_{CH,\,CX}$ [c]		8.4	7.1	5.3	6.2	3.1	−2.6	1.0	−0.1	3.7
	LPO[d]		18.5	15.9	−11.8	−25.4	−49.1	−50.6	−27.2	−45.7	−14.2
	$\Sigma\sigma^{p}_{xx}$		36.6	31.5	−13.7	−37.0	−74.1	−90.3	−47.0	−79.8	−27.1
yy	σ_{CO}	π^*	−551.3	−515.5	−484.3	−440.9	−447.2	−408.6	−373.9	−375.4	−348.0
	π_{CO}	σ^*	−184.5	−170.0	−164.3	−165.6	−158.6	−134.9	−134.0	−137.2	−142.5
	$\sigma_{CH,\,CX}$ [c]	π^*	−39.2	−31.3	−32.1	−33.1	−32.3	−26.6	−27.1	−26.1	−25.8
	LPO (n′)[d]	π^*	−221.0	−207.9	−188.1	−165.0	−179.9	−153.2	−131.0	−130.9	−120.3
	$\Sigma\sigma^{p}_{yy}$		−998.6	−924.5	−871.4	−810.8	−826.0	−728.1	−673.5	−675.7	−637.9
zz	σ_{CO}		−0.8	0.0	0.0	−2.2	−4.8	0.0	−0.4	−0.7	0.0
	π_{CO}	σ^*	−124.0	−81.9	−61.3	−82.0	−69.3	0.1	−11.4	1.4	−10.5
	$\sigma_{CH,\,CX}$ [c]	π^*	−157.6	−107.5	−94.8	−105.4	−94.9	−45.0	−48.0	−47.6	−55.1
	LPO (n)[d]	π^*	−1766.4	−1378.6	−1194.4	−1061.8	−960.9	−654.9	−654.5	−622.7	−645.2
	$\Sigma\sigma^{p}_{zz}$		−2055.4	−1568.2	−1354.9	−1274.6	−1146.3	−703.3	−725.2	−673.7	−714.4
	σ^{p}_{iso} [e]		−1005.2	−820.3	−746.6	−707.5	−682.2	−507.2	−481.9	−476.4	−459.8

[a] Occupied orbital.
[b] Virtual orbital (supposed).
[c] Sum of σ_{CH} and σ_{CX}.
[d] Lone pair orbitals.
[e] $\sigma^{p}_{iso} = (\sigma^{p}_{xx} + \sigma^{p}_{yy} + \sigma^{p}_{zz})/3$.

furnish a more important contribution to σ_{yy} of ^{17}O than the n′ orbital, although it is lower in energy; this is also the case for σ_{yy} of ^{13}C. The same result had been obtained in several *ab initio* calculations (IGLO, LORG) of related carbonyl compounds.[18,19,57] On the other hand, as expected, the contribution of the n–π^* excitation (smaller energy gap) to σ_{zz} is greater than that of n′–π^* (larger energy gap) to σ_{yy}. In the σ_{xx} component of ^{17}O, finally, there exists for **2** no deshielding σ^{p}_{xx} part from any available occupied orbital. These last statements refer to a strictly localized description.

For ^{13}C of **2**, the only important contribution to the deshielding component σ^{p}_{zz} comes from the σ_{CH} ground-state orbital, which suggests a σ_{CH}–π^*_{CO} excitation. In the σ^{p}_{yy} deshielding component of ^{13}C of **2**, the major contribution (63%) is associated with the σ_{CO} occupied orbital, suggesting the σ_{CO}–π^*_{CO} excitation for the required *z*,*x* charge circulation. Of the less contributing occupied orbitals, one can cite $\sigma_{\mathrm{CH,\,CX}}$ (the one with the lobe in the *z* direction) for the $\sigma_{\mathrm{CH,\,CX}}$–$\pi^*_{\mathrm{CO}}$ excitation, and further π_{CO} for the π_{CO}–σ^*_{CO} excitation, and LPO (n′, with the lobe in the *z* direction) for the n′–π^*_{CO} excitation. For the σ^{p}_{xx} component of ^{13}C of **2**, finally, there are only two modest deshielding contributions, suggesting the σ_{CO}–σ^*_{CH} and σ_{CH}–σ^*_{CO} excitations, both in the *y*,*z* plane.

Compounds 1–9

Comparing the components of deshielding σ^{p}_{ii} for **1**–**9**, one finds for ^{17}O (Table 5) that the principal deshielding component σ^{p}_{zz} strongly decreases from X = SiH_3 to X = OH (Table 3 and Fig. 3 had shown this same effect for the total shielding σ_{zz} ; the close parallelism between the total shielding component σ_{zz} and its deshielding part σ^{p}_{zz} confirms that the diamagnetic term σ^{d} is fairly constant). For each ground-state orbital of **1** and **3**–**9**, we admit the same excitations as in **2**. The decrease of σ^{p}_{zz} on going from **1** to **9** is attributed to the LPO orbital n; as for **2**, we admit that this is essentially due to the n–π^*_{CO} transition, as all other excitations starting from LPO and presenting the required symmetry type need far higher energies. It is well known that when in HCOX the electron-donating power of X is increased, the HOMO–LUMO gap (n–π^*) becomes larger (as manifest in the UV spectra), by lowering the energy of the n orbital and also by increasing that of π^*.[40,42] This energy increase diminishes the importance of the deshielding σ^{p}_{zz} component, until σ^{p}_{zz} becomes equal (for X = OH) to σ^{p}_{yy}, and the total shielding component σ_{zz} equal to σ_{yy} (Fig. 3). It constitutes the principal contribution to the effect of substituent X on the ^{17}O shielding. Table 5 shows that the deshielding contributions of the other localized orbitals, notably the $\sigma_{\mathrm{CH,\,CX}}$ and the π_{CO} orbitals (excitations $\sigma_{\mathrm{CH,\,CX}}$–$\pi^*_{\mathrm{CO}}$ and π_{CO}–$\sigma^*_{\mathrm{CH,\,CX}}$, respectively), also decrease from **1** to **9**, but much less than that of LPO. For $\sigma^{\mathrm{p}}_{yy}(^{17}\mathrm{O})$ also, the influence of X upon the σ_{CO}, LPO and π_{CO} occupied orbitals (excitations σ_{CO}–π^*_{CO}, n′–π^*_{CO} and π_{CO}–$\sigma^*_{\mathrm{CH,\,CX}}$, respectively) diminishes between **1** and **9**, most strongly σ_{CO}–π^*_{CO}; again, each of these transitions, as well as their sum, diminishes less than LPO (i.e. n–π^*_{CO}) for σ^{p}_{zz}. Finally, the σ^{p}_{xx} component, with its deshielding contribution small compared with the two other directions, shows only a small influence by the group X.

For ^{13}C (Table 4), the major deshielding component, σ^{p}_{yy}, also diminishes from **1** to **9**. For this component, the main localized orbital is the σ_{CO} bond, active probably mostly via the σ_{CO}–π^*_{CO} excitation, which is seen to diminish with changes of X. The $\sigma^{\mathrm{p}}_{zz}(^{13}\mathrm{C})$ deshielding component also diminishes from **1** to **9**, although less (and less regularly) than σ^{p}_{zz} for ^{17}O. For $\sigma^{\mathrm{p}}_{zz}(^{13}\mathrm{C})$, the $\sigma_{\mathrm{CH,\,CX}}$ localized orbital yields the only deshielding contributions; between **1** and **9**, σ_{CH} and σ_{CX} change in virtually the same way (not shown in Table 4),[36] each contributing about half of the sum $\sigma_{\mathrm{CH,\,CX}}$ (Table 4); the $\sigma_{\mathrm{CH,\,CX}}$–$\pi^*_{\mathrm{CO}}$ excitation is of appropriate symmetry. As before, both transitions mentioned use the π^*_{CO} unoccupied orbital, which brings in substituent sensitivity. In contrast to σ^{p}_{zz} of ^{17}O, the LPO orbital, i.e. the n–π^*_{CO} transition, has no importance for the σ^{p}_{zz} component of ^{13}C in general, and for its substituent sensitivity in particular. Finally, the σ^{p}_{xx} component, again, does not change with variation of X.

For σ_{yy} of ^{13}C and of ^{17}O, most of the deshielding contributions mentioned above involve the π^* virtual orbital. It is tempting to speculate whether the decline of the deshielding components σ_{yy} (Tables 2 and 3) in the series **1**–**9** can be related to the simultaneous increase in the energy level of π^*.

This analysis confirms that the difference between the total shielding σ of ^{17}O and ^{13}C, mainly situated in the σ_{zz} component, is due to the importance of the LPO, i.e. the n–π^*_{CO} excitation for ^{17}O, and its absence for ^{13}C. This, of course, is not a surprise: the n orbital is essentially situated on oxygen. As the energy of the n–π^*_{CO} excitation increases with increasing resonance donation by the substituent X, the deshielding contribution of the σ^{p}_{zz} component decreases.

The n–π^* excitation is not the only one which, by its unilateral position, acts preferentially upon one of the atoms of the carbonyl group: the n′–π^*_{CO} transition also, although much less important than n–π^*_{CO}, is much more active on ^{17}O than on ^{13}C; on the other hand, the $\sigma_{\mathrm{CH,\,CX}}$ orbital, situated mainly on C, is found to be much more active on ^{13}C (particularly σ^{p}_{zz}, presumably via the $\sigma_{\mathrm{CH,\,CX}}$–$\pi^*_{\mathrm{CO}}$ excitation) that on ^{17}O. By the same token, the σ_{CO} and π_{CO} orbitals, the ground states of the σ_{CO}–π^*_{CO} and π_{CO}–σ^*_{CO} excitations, respectively, are common to both atoms and are active both on ^{17}O and on ^{13}C deshielding (both in σ^{p}_{yy}).

As mentioned above, σ^{p}_{yy} is the strongest deshielding component not only for ^{13}C of carbonyl groups, but also for other π-systems such as olefins and imines; it remains to be established whether there is an analogy of the contributing excitations also. Actually the carbonyl oxygen owes its exceptional shielding character, the prevalence of the σ^{p}_{zz} deshielding component and its substituent sensitivity to the availability of the low-lying n–π^*_{CO} excitation, acting upon this component. In its absence (carbonyl oxygen in the presence of strong resonance; ^{13}C of carbonyl, imine and olefin groups) the σ^{p}_{yy} component becomes the most important, via excitations which are less sensitive to substituent effects. In the same way as ^{17}O in the carbonyl compounds, ^{15}N in imines[27,43] and ^{31}P in iminophosphines RP=NR[44] show the particular prevalence of the n–π^* excitation for deshielding and substituent influence.

para-Substituted benzoyl compounds: the 'reverse' substituent effect upon $\delta(^{13}C)$ of the carbonyl carbon

Another way to test the action of electron-donating and -attracting substituents on ^{13}C and ^{17}O of carbonyl compounds is to vary the *para* substituent in p-YC_6H_4COX compounds (benzaldehydes, acetophenones, etc.). With varying Y, these compounds show in ^{17}O NMR a clear linear dependence of the chemical shift value $\delta(^{17}O)$ upon the donating or attracting power of Y.[2,45,46] This includes not only electron donors Y (as above in the case of the variation of X in HCOX), but also electron attractors (e.g. NO_2, CN, CF_3). In all different classes of YC_6H_4COX (X as above for HCOX), the linearity of the dependence expresses itself in well behaved correlations ($r \geqslant 0.98$) of $\delta(^{17}O)$ with, e.g., the Hammett–Brown substituent parameter σ^+ of Y.[2]

In ^{13}C NMR, in contrast, the influence of the substituent Y of p-YC_6H_4COX upon $\delta(^{13}C)$ of the carbonyl carbon is small;[47] the range of the shift values between Y = MeO and Y = NO_2 is only *ca.* 1 ppm for acetophenones (Table 6) and for benzamides, a small fraction of that found for ^{17}O (see below). Furthermore, in contrast to ^{17}O, the substituent effect upon $\delta(^{13}C)$ is mostly not linear with the donor/acceptor properties of Y, but often the shielding is lowest with Y = H, and both electron-donating and -attracting substituents increase it (which points to an inductive effect[47]). The electronic effect which conditions that part of the curve in which electron-donating substituents Y decrease the shielding has been called reverse substituent effect. The term 'reverse' clearly refers to the authors' idea that only electron density [the ΣQ term of Eqn (2)] determines the shielding. The 'reverse' effect has been found in other cases of side-chains of aromatic compounds, e.g. $\delta(^{15}N)$ in substituted nitrobenzenes[48] and $\delta(^{13}C)$ in benzonitriles,[49,50] although cases of truly linear 'reverse' dependence seem to be rare in sp^2-type systems. To explain the 'reverse' relationship in NMR correlations on the basis of the bond order–charge density term of Eqn (2) alone, a particular inductive effect, π-polarization, acting alongside the well established classical field inductive effect, has been put forward.[51] We are not aware whether this effect has been invoked outside the interpretation of NMR spectra.

Table 6. Substituent effects on ^{13}C and ^{17}O shift values of *para*-substituted acetophenones p-YC_6H_4COMe (shift differences $\Delta\delta$, in ppm from Y = H; higher shielding negative)

Y	$\Delta\delta(^{13}C)$[a]	$\Delta\delta(^{17}O)$[b]
NH_2	−1.6	−33.0
OMe	−1.2	−17.8
Me	−0.3	−8.1
F	−1.7	−3.5
H	0	0
Cl	−1.4	2
Br	−1.1	2.9
COMe	−0.6	12.8
CF_3	−1.2	13.7
CN	−1.5	18.2
NO_2	−1.7	21.3

[a] Data from Ref. 47.
[b] Data from Ref. 64.

We think that, at least in the case of the benzoyl compounds, the NMR substituent effects observed can be explained in a different way, by taking into account the electronic excitation term ΔE^{-1}. We admit that, as was the case with the HCOX compounds, here too the n–π^*_{CO} transition is the most important contributor to the isotropic (de)shielding of ^{17}O, and that the corresponding energy gap is subject to the effect of conjugation with donor and acceptor substituents. As the n orbital is nearly exclusively situated on the O atom and very little on C, it contributes little, if at all, to the deshielding of ^{13}C. The latter is then determined by the less substituent-dependent transitions mentioned above. Thus the substituent Y in YC_6H_4COX has a strong and linear action on the shielding of ^{17}O, comparable to that which the substituent X exerts in HCOX (i.e. on σ^p_{zz}), whereas in both cases the substituent sensitivity of σ^p_{yy}, passing through less effective transitions, is counteracted by other influences, e.g. the habitual inductive effect. As a consequence, it is not necessary to refer to special electronic effects to explain the irregularity of the substituent effects upon ^{13}C of the carbonyl group. It remains to be examined whether similar explanations also hold for other cases of 'reverse' substituent effects.

The case of the *para*-substituted benzoyl cations $Ar{-}C{\equiv}O^+$

As mentioned above, the oxygen atom of benzoyl compounds p-YC_6H_4COX is subject to the 'normal' influence of electron-donating and -attracting substituents Y; the substituent sensitivity of $\delta(^{17}O)$, expressed, for instance, by the range between Y = OMe and Y = NO_2, has been found to be determined by the character of X.[2] The lower the electron-donating power of X, i.e. the greater the electron deficiency at the carbonyl group, the greater is the influence of Y upon $\delta(^{17}O)$: for benzaldehydes (X = H) the range is 48 ppm, whereas for benzamides (X = NH_2) it is only 12 ppm; of course, this relationship can also be expressed in terms of Hammett-type ρ values, in particular ρ^+.[2]

It therefore came as a surprise when Olah *et al.*[52] discovered that in aroyl cations, where the electron deficiency at the site of the CO group is greatest, the shift value of ^{17}O is (nearly) independent of substituents in *para* and *meta* positions. On closer inspection one notes that p-MeO as well as p-CF_3 groups have a slight deshielding action upon $\delta(^{17}O)$, but only *ca.* 2 ppm. This interesting observation (as well as the observation of a 'reverse' substituent effect upon the ^{13}C shifts of the same compounds[53]) can, however, be rationalized by an extension of the arguments given above for ^{13}C of sp^2-type carbonyl compounds.

In acyl cations $RC^+{=}O$ (**A**) $\leftrightarrow$ $RC{\equiv}O^+$ (**B**), the resonance form **B** prevails, thus the compounds are (ideally) linear and show (of course depending on R) $C_{\infty v}$ symmetry. In contrast to sp^2-type carbonyl compounds, the sp-bound oxygen atom possesses no high-lying localized n orbital with the predominant lobe perpendicular to the C—O bond (but only an n′ orbital with the lobe in the C—O direction); in its absence, the n–π* transition, characteristic of RCOX compounds and responsible for their large deshielding as well as for significant substituent effects upon ^{17}O of acyl compounds, can no longer exist. This is manifest also in the UV spectra: in $MeCO^+$ there is no absorption >215 nm,[54] instead of *ca.* 250 nm in MeCHO. If we continue to designate the C—O direction as the *z*-axis, an electron circulation in the plane perpendicular to this axis must be magnetically inactive, because of the degeneracy of the π orbitals. As a consequence, the paramagnetic part of the shielding in the *z* direction, $\sigma_{\parallel}{}^{p}$ is zero and the shielding $\sigma_{\parallel}$, now consisting only of the diamagnetic part σ^d, is expected to approach the value of the isolated atom σ^d(atom).

The IGLO program, executed for the simplest model compound HCO^+ (and also for $MeCO^+$, not shown here[36]), furnishes the paramagnetic deshielding components of $\sigma_{\perp}{}^{p}$ as the sum of the contributions of the occupied orbitals σ_{CO} (direction: *z*), π_{CO} (direction: $x = y$), σ_{CH} (direction: *z*) and LPO (direction: *z*) (Table 7). The three ground-state orbitals of direction *z* will combine with virtual orbital π^*_{CO}, yielding magnetic moments in the $x(=y)$ direction; the π_{CO} occupied orbital can combine with the σ^*_{CO} or σ^*_{CH} virtuals orbitals. All four circulations yield the $\sigma_{xx} = \sigma_{yy} = \sigma_{\perp}$ component of (de)shielding. It turns out (Table 7) that, for ^{13}C as for ^{17}O, the σ_{CO}–π^*_{CO} contribution is the most important one, followed by σ_{CH}–π^*_{CO} (for ^{13}C) and LPO–π^*_{CO} (for ^{17}O); here again, the localization of the occupied orbital determines which atom is most influenced. On the other hand, for the $\sigma_{\parallel}$ component of HCO^+ there is no deshielding contribution (not shown in Table 7), and the calculated values of $\sigma_{\parallel}$ are close to σ^d(atom) of the isolated O atom (see above);[55] for instance, for HCO^+ $\sigma_{\parallel}(\text{calc}) = 412$ ppm,[36] $\sigma(\text{atom})(^{17}O) = 395$ ppm.[38] At the same time, owing to the disappearance of one of the deshielding paramagnetic contributions, the isotropic shielding value is particularly high: for HCO^+ shift values $\delta(\text{IGLO})(^{13}C) = 132$ ppm and $\delta(\text{IGLO})(^{17}O) = 338$ ppm are calculated, in agreement with measured shift values $\delta(^{13}C)(MeCO^+) = 150$ ppm and $\delta(^{17}O)(MeCO^+) = 299$ ppm (Table 7).[56] These values are *ca.* 40 and *ca.* 200 ppm, respectively, more shielded than in aldehydes and ketones [in spite of the presence of a positive charge on O, which, through the radius term r^{-3} of Eqn (2), should have the opposite effect upon $\delta(^{17}O)$].

Table 7. Main orbital paramagnetic contributions σ^p to the $\sigma_{\perp}$ component ($=\sigma_{xx} = \sigma_{yy}$) of the ^{13}C and ^{17}O shielding tensors in $HC{\equiv}O^+$ (in ppm, higher shielding positive)

	^{13}C	^{17}O
σ_{CO}	−332.2	−614.3
π_{CO} [a]	−41.8	−179.1
σ_{CH}	−191.0	−56.1
LPO[b]	−50.7	−415.5
$\Sigma\sigma_{\perp}{}^{p}$	−615.7	−1265.0
σ^p_{iso} [c]	−205.2	−421.7
σ^d_{iso}	259.1	391.7
σ_{iso} [d]	53.9	−30.0
δ(IGLO)	131.6	337.9
δ(exp)[e]	150	299

[a] Sum of the two π orbitals.

[b] Lone pair orbital.

[c] $\sigma^p_{iso} = \Sigma\sigma_{\perp}{}^{p}/3$; $\Sigma\sigma_{\parallel}{}^{p} = 0$.

[d] $\sigma^p_{iso} + \sigma^d_{iso}$.

[e] For $MeCO^+$; Ref. 56.

For $PhCO^+$, the measured shift values are $\delta(^{13}C) = 155$ ppm[53] and $\delta(^{17}O) = 318$ ppm,[52] again not far from $\delta(\text{IGLO})(HCO^+)$. In this compound, the original $C_{\infty v}$ symmetry of HCO^+ is diminished to C_{2v} by the presence of the aromatic ring. Consequently, the *x,y* degeneracy disappears, i.e. $\sigma_{xx} \neq \sigma_{yy}$; the effect, however, would be expected to be rather small. This expectation is borne out in the isoelectronic benzonitriles $ArC{\equiv}N$, in which the two components of $\sigma_{\perp}$ differ by only *ca.* 10 ppm (^{15}N) and *ca.* 30 ppm (^{13}C), respectively.[50]

In the absence of the action of the n–π* excitation, which, as has been shown, would furnish a substituent-sensitive contribution of deshielding, the most important deshielding contribution to $\sigma(^{17}O)$ is that coming from the σ_{CO}–π^*_{CO} transition, with the magnetic moment perpendicular to the C—O bond. In the preceding examples of ArCOX, the corresponding transition had been found to be less influenced by the resonance effect of substituents, and only slightly by inductive effects; hence we can admit that this is the case with the benzoyl cations also, just as had been observed.

In transition metal carbonyl complexes, the difference between linear terminal groups in MCO and bridge groups in M_2CO corresponds formally to that between RCO^+ and R_2CO. For the linear groups, a close analogy of the shielding characteristics seems to exist, in the proximity of the values of σ_{iso} as well as of the shielding tensor components for ^{13}C and ^{17}O, e.g. in $Cr(CO)_6$, and even in the relative importance of the individual orbital contributions.[10,57] For the bridging systems,[58] the similarity between R_2CO and M_2CO is less evident; this might be due to differences in the molecular geometry.

CONCLUSIONS

In carbonyl compounds HCOX and *p*-YC_6H_4COX, substituents X and Y, respectively, influence the ^{17}O much more than the ^{13}C NMR signals. This difference has been attributed to the n–π^*_{CO} excitation. As the n orbital is essentially situated on the oxygen atom, electronic modifications of the energy of this excitation affect primarily ^{17}O. It would be interesting to extend this type of analysis to apparently related cases of divergence of NMR behaviour of neighbouring atoms, e.g. the difference between C-α and C-β of olefins, styrenes and acetylenes.

EXPERIMENTAL

Calculations

In chemical shift calculations, IGLO basis II was used[11] [(9s, 5p) Huzinaga set in the contraction (5, 4 × 1; 2, 1, 1, 1) augmented by one set of d-function for the second-row atoms B–F and 5s augmented by one p set for H]. Geometries were fully optimized by using the 6–31G** basis set and standard convergence criteria (Program Spartan 3.1; Wavefunction, Irvine, CA, USA), yielding the following $C{=}O$ distances and OCX angles: **1**, 1.1936 Å, 122.7°; **2**, 1.1844 Å, 122.2°; **3**, 1.1877 Å, 124.4°; **4**, 1.1801 Å, 125.1°; **5**, 1.1652 Å, 123.2°; **6**, 1.1640 Å, 123.0°; **7**, 1.1919 Å, 125.0°; **8**, 1.1835 Å, 125.7°; **9**, 1.1819 Å, 124.9°; and **10**, 1.2314 Å, 131.0°.

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