NMR of Terminal Oxygen. Part 7.[1] ^{17}O NMR Spectra of Benzoyl Derivatives of Ge, Se, Te and I: π-Bond Order and Excitation Energy in Benzoyl Compounds

Hans Dahn* **and Péter Péchy**†
Institut de Chimie Organique de l'Université, Rue de la Barre 2, CH-1005 Lausanne, Switzerland

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The benzoyl derivatives of SeR, TeR and I show lower field ^{17}O NMR signals than those of the lighter elements in the same group of the Periodic Table, whereas ArCOGeR$_3$ is as low-field as ArCOSiR$_3$. The δ_O values of 14 types of benzoyl compounds ArCOX are discussed in terms of π-bond order (obtained from arene substituent sensitivities using the 'tool of increasing electron demand') and of electronic excitation energy (obtained from UV spectra). It is concluded that, for ^{17}O NMR, the terms ΔE^{-1} and ΣQ of the Karplus–Pople equation are, at least to a certain degree, independent of one another.

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^{17}O NMR chemical shifts, particularly of π-bonded oxygen, are very sensitive to structural and electronic influences.[2,3] In benzoyl compounds (ArCOX) the δ_O values have been found to vary over a large part of the spectral window, from *ca.* 100 ppm (high field) to 700 ppm.[3] The shift depends very strongly upon X, particularly on the nature of the atom directly bound to the carbonyl group. The latter has been varied among the elements of the second[4] (C, N, O, F) and third[4,5] (Si, P, S, Cl) period of the Periodic Table, and characteristic changes have been found (Table 1). As the n-donor effect of atoms X diminishes with increasing bond length, when descending within a group of the Periodic Table, the shift values of the attached carbonyl oxygen increase significantly. We have now extended the scope of atoms for which benzoyl derivatives have been measured, by including fourth- (Ge, Se) and fifth-row atoms (Te, I), in order to see whether a limiting value would be attained with higher elements. The result was expected to allow amplification of the chemical interpretation.

Results

For reasons of convenience some of the alkyl groups bound to the heteroatoms in the compounds RCOX were different from methyl. It has been shown, however, that the influence of this group, which is two bonds distant from –CO–, is quite small; for instance in the series of HCO–OR one finds for R = Me, Et, Pr δ_O = 361, 359 and 354 ppm respectively.[2]

We have measured (known) benzoyl derivatives of alkyl-Ge, alkyl-Se, alkyl-Te, and I, and found the following δ_O values (in parentheses: line width): PhCOGeMe$_3$ 665.8 ppm (380 Hz); PhCOSeMe 525.2 ppm (270 Hz); PhCOTeBu 591.8 ppm (390 Hz); PhCOI 571.0 ppm (200 Hz).

It is significant that all new δ_O values were found in the low-field region of the spectral window, most of them not far from the values of benzaldehyde (562 ppm) and acetophenone (549 ppm).

Discussion

In general, the origin of the chemical shifts of the higher nuclei, including C and O, is not fully understood. An approximation given by the Karplus–Pople[6] equation (1) uses three parameters to define the (preponderant) paramagnetic contribution σ_p to the shielding: the 'average' electronic excitation energy ΔE, the p-orbital radius r, and a bond order–charge density term ΣQ.

$$\sigma_p = \text{const.}(\Delta E^{-1})(r^{-3})(\Sigma Q) \qquad (1)$$

Table 1 Acyl compounds RCOX: ^{17}O NMR chemical shifts δ_O (R = Ph; in MeCN); arene substituent sensitivities ρ^+ (R = 4-YC$_6$H$_4$; in MeCN), and UV absorptions (n ⟶ π*) (R as indicated; in alkane solution)

	Group				
	1	14	15	16	17
X	H[a]	CMe$_3$[b]	NMe$_2$[b]	OMe[a]	F[a]
δ_O(ppm)	562	563	345	337	353
ρ^+	26	22[c]	7[d]	8	14
λ_{max}(nm)	290	287[e]	207[e]	210[e]	205[e]
X		SiMe$_3$[b]	PPh$_2$[b]	SEt[a]	Cl[a]
δ_O(ppm)		681	609	489	484
ρ^+		29	24	16	20
λ_{max}(nm)		371,[e] 424[f]	371,[g] 390[h]	266[i]	241[e]
X		GeMe$_3$		SeMe	Br[a]
δ_O(ppm)		666[i]		525[i]	513
ρ^+					24
λ_{max}(nm)		366,[k] 417[f]		297[i]	250[e]
X				TeBu	I
δ_O(ppm)				592[i]	571[i]
λ_{max}(nm)				346[i]	

[a] Data from ref. 4. [b] Data from ref. 5. [c] Value for X = Me, from ref. 4. [d] Value for X = NH$_2$, from ref. 4. [e] Value for R = Me, from ref. 16. [f] Value for R = Ph, from ref. 16. [g] Value for R = Me, X = PPh$_2$, from ref. 24. [h] Value for R = Ph, from ref. 24. [i] R = Ph, this work. [k] Value for R = Me, X = GePh$_3$, from ref. 16.

Intuitively one is tempted to think that these terms are not really independent of one another, but this has been neither proved nor disproved for ^{17}O NMR data. Until now correlations of measured shift values δ_O have been established with only one of the three terms at a time: (*a*) The term ΔE, experimentally approximated by the lowest-lying (n ⟶ π*) UV absorption;[3a,7] or (*b*) the term ΣQ, in π-systems approximated as the π-bond order, sometimes calculated,[8] or occasionally evaluated from nuclear quadrupole resonance (NQR) measurements.[8,9] For carbonyl compounds the effects of substituents in the arene ring of acetophenones have been shown to depend upon the (calculated) π-bond order,[10] more than upon λ_{max};[11] Cheng *et al.*[12] have confirmed, by an analysis of NQR data, that the bond order term is the dominant factor influencing the ^{17}O shift values of a series of compounds PhCOX (X = H, Ph, F, Cl, OR, O$^-$). As to the second variable of eqn. (1), the radius of the p-orbital on O, it is particularly difficult to evaluate; it has been supposed to be included in the

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† On leave from the Technical University of Budapest.

evaluation of one of the two other terms, preferentially the π-bond order term.[10]

We have recently shown[4] that the arene substituent sensitivity of benzoyl compounds can be used as a measure of the electronegativity of carbonyl groups and of the influence of n-donors upon it. To do this, the 'tool of increasing electron demand', developed[13] to characterize carbenium ion centres, has been applied to carbonyl compounds. In this case the 'tool' implies that the less the electron deficiency of a carbonyl group –CO–X is diminished by resonance donation from X, the more any (spectral or other) carbonyl property will be sensitive to other substituents, notably substituents in the arene ring. The ^{17}O shift values are particularly appropriate for application of the 'tool' (quite in contrast to ^{13}C spectra; the latter often show an inverse substituent effect, electron donating substituents *diminishing* the shielding). The arene substituent sensitivity, as usual measured by the Hammett–Brown coefficient ρ^+, varies considerably from one COX group to another. In the absence of n-donation, as in benzaldehydes and acetophenones, ρ^+ = 26 and 22 respectively; it is 29 for the still more electron-demanding ω,ω,ω-trifluoroacetophenones.[4] In the presence of electron donating groups, which diminish the electron demand of the carbonyl group, the substituent sensitivity ρ^+ is lowered: –COCl 20, –COF 14, –COOMe 8, –CONH$_2$ 7, –COO$^-$ 5.[4] The ρ^+ values thus parallel the chemical electrophilicities of the carbonyl groups, which are qualitatively very well known from chemical reactivities, but which had not previously been classified numerically. On the other hand the electron demand of the carbonyl group, accessible *via* the 'tool' and expressed as ρ^+, is clearly related to the π-bond order; we use ρ^+ as an experimental measure approximating the ΣQ term of eqn. (1).

It turned out[4] that, for –COX with donor groups X, the individual shift values of the unsubstituted benzoyl compounds PhCOX are correlated with the ρ^+ values of the series. For aldehydes and ketones, in the absence of resonance interaction of CO with X, the δ_O values are *ca.* 550 ppm; they move upfield as X becomes electron donating, *e.g.* –COCl 491, –COF 353, –COOMe 337, –CONH$_2$ 326, –COO$^-$ 265 ppm.[4] On the other hand if X is an electron attractor, like CF$_3$, which increases the electrophilicity ρ^+, the shift value is not much changed (554 ppm).[4] The correlation between δ_O and ρ^+ has been interpreted as a sign of the preponderance of the bond-order term of eqn. (1);[4] with the more comprehensive data set now available (in total >120 compounds) we can try to evaluate, at least qualitatively, the influence of other parameters, notably the ΔE term of eqn. (1).

In group 14 of the Periodic Table (C, Si, Ge), n-donation from X to CO is of course absent, *i.e.* the bond order term is relatively unimportant; this is confirmed by the similarity of the ρ^+ values for the SiMe$_3$ compounds with those of aldehydes and ketones (its small increase might come from the known[14] electron attraction by the SiMe$_3$ group, as in the case of CF$_3$). The δ_O values, however, are ≥100 ppm downfield from the corresponding ketone (563 ppm) and the trifluoromethyl ketone (554 ppm). This effect can be attributed to changes in the ΔE term of eqn. (1): the yellow Si- and Ge-ketones show their lowest-energy electronic absorption band *ca.* 90 nm red-shifted from their C-analogues (Table 1).[14a] The IR spectra confirm the parallelism of δ_O and λ_{max}: PhCOCPh$_3$ 1692 cm^{-1}, PhCOSiPh$_3$ 1618 cm^{-1}, PhCOGePh$_3$ 1629 cm^{-1}.[14b] The UV and IR spectroscopic particularities of silyl ketones have been the object of a voluminous literature.[14,15] The decrease of the excitation energies has been attributed to considerably enhanced ground state energies plus slightly lowered first excited states.[16] The former has been explained by a transfer of electron density from CO to Si, either by induction[17] or by electron back donation[18] (the second mechanism involves a d-orbital on Si, a rather controversial argument).[19] The direction of this electron movement agrees with the observed deshielding of O.

At the other extreme, the benzoyl compounds of group 17 elements (benzoyl halides) show an even stronger deshielding than those of group 14: $\Delta\delta_O$ = 218 ppm in going from F to I; but the smaller difference in their n ⟶ π* absorption[16,20] (Table 1), confirmed by IR frequencies [MeCOX (cm^{-1}): F 1841, Cl 1806, Br 1802, I 1799],[20] is scarcely sufficient to explain it. Furthermore, contrary to group 14, inductive electron attraction cannot be responsible here, because it diminishes from F to I. However, in this group there is a regular increase of the ρ^+ values from F to Br (14 to 24), indicating a parallel change in the π-bond order with diminishing n-donation from X, which may account for the deshielding. The analysis of the NQR values of PhCOF and PhCOCl supports this view,[12] as does the increase of chemical reactivity from RCOF to RCOI.[21] The δ_O value of PhCOI is close to that of aldehydes and ketones, suggesting that n-donation is no longer effective, presumably due to the enhanced C–X distance.

For the compounds of group 16 (O, S, Se, Te), both the ΔE term and the π-bond order term seem to cooperate to yield the observed deshielding of (totally) $\Delta\delta_O$ = 255 ppm. The UV spectra (Table 1; Se and Te acyl compounds had, to our knowledge, not been measured previously in the UV region) show a rather regular red-shift from –COOR (210 nm) to –COTeR (346 nm); the trend is confirmed by decreasing IR frequencies [2-MeOC$_6$H$_4$COX (cm^{-1}): OMe 1700, SMe 1670, SeMe 1630, TeMe 1627].[22] At the same time ρ^+ increases from 8 to 16 in going from OR to SR, as does the chemical activity; the decrease of M-donating power OR > SR > SeR > TeR has also been established, *via* their arene substituent effects σ.[23] It is at present not possible to evaluate the relative importance of the two terms contributing to the observed deshielding.

The same can be claimed for the two series of compounds measured in group 15 of the Periodic Table, which exhibit a particularly important deshielding in going from N to P: $\Delta\delta_O$ = 260 ppm.[5] The UV spectra show, from amides to phosphides, a red-shift of 160 nm,[24] *i.e.* a diminished ΔE term; at the same time the π-bond order increases, indicated by ρ^+ rising from 7 to 24.[5] For the –COPR$_2$ group the proximity of the δ_O and ρ^+ values to those of aldehydes and ketones confirms the absence of resonance, which is also manifest for instance in the absence of coplanarity[25] and in increased chemical reactivity.[24] The δ_O value of 609 ppm, more deshielded than aldehydes and ketones, combined with low excitation energy, can be interpreted, as above, as a sign of electron transfer in the opposite direction, *i.e.* from CO to P.

Comparing the values for the different groups (Table 1), one is tempted to speculate that group 15 is closer to 14 (excepting for resonance in –CONR$_2$) and group 16 closer to 17. For instance, the non-resonance limiting δ_O and ρ^+ values of aldehydes and ketones are attained in groups 14 and 15 in the third period (Si, P), in groups 17 and 16 in the fifth period (I, Te). Whether this means that in group 15 the variation of the ΔE term and in group 16 that of the bond order term is of more importance in determining the shifts, must be left an open question.

Conclusion

To evaluate the ^{17}O shift values of 14 types of benzoyl compounds ArCOX, we have estimated the ΔE term of eqn. (1), as usual, by the low-lying n ⟶ π* electronic excitation energy; the bond order term of eqn. (1) has been approximated by the π-bond order, evaluated (using the 'tool of increasing electron demand') from the sensitivity ρ^+ of the chemical shifts δ_O to arene substituents; the p-orbital radius term of eqn. (1) has been neglected (or finds itself incorporated in the experimental evaluation of one of the other two terms). It is found that in the series X = F, Cl, Br, I, variation of δ_O is essentially determined by variation of the π-bond order, caused by the diminishing electron donation from X to CO, whereas in the series X = CR_3, SiR_3, GeR_3, the ΔE term is prevalent (the observed deviation might coincide with increasing inductive electron transfer from CO to X). In the two intermediate series, X = NR_2, PR_2, and X = OR, SR, SeR, TeR, variation of both terms are working in the same direction of deshielding O, without a clear separation being possible for the moment.

The result confirms that, for ^{17}O NMR, the excitation energy term and the bond order term of the Karplus–Pople equation are, to a certain degree at least, independent of one another.

Experimental

^{17}O NMR spectra were recorded on a Bruker WH-360 spectrometer equipped with a 10 mm probe at 48.8 MHz in the Fourier transform (FT) mode without lock. System control, data acquisitions and data managements 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; 1.4–2.3 M scans; measurements were made with sample spinning (27 Hz). An even number (28–32) left-shifts (LS) were applied to the FID signal; the latter was zero-filled to 8 K words, and exponentially multiplied with a 100 Hz line-broadening factor (LB) before being subjected to the FT. The chemical shifts, measured in *ca.* 0.4 mol dm^{-3} MeCN solution at 40 °C, are reported relative to $\delta(H_2O) = 0.00$ ppm; dioxan ($\delta = 0.0$ ppm) was used as an external standard; downfield shifts are positive. The general reproducibility of chemical shift values is *ca.* ± 1 ppm (± 0.2 ppm within the same series).

^1H NMR spectra were recorded with a Bruker AC-250 or Bruker WP-80 spectrometer, ^{13}C NMR spectra with a Bruker AC 250. IR spectra were run on a Perkin-Elmer 1420. UV spectra were recorded with a Hewlett-Packard 8450A.

Compounds.—Trimethyl benzoylgermane.[17] This compound was prepared by the method used for the ethyl analogue[26] *via* 2-trimethyl-2-phenylgermyl-1,2-dithiane, which showed m.p. 90–93 °C [$\nu_{max}(CHCl_3)/cm^{-1}$ 1589 and 1488; $\delta_H(CDCl_3)$ 0.19 (s, 9 H), 1.8–2.85 (m, 6 H) and 7.1–7.9 (m, 5 H)]. New spectral data of trimethyl benzoylgermane: $\delta_H(CDCl_3)$ 0.52 (s, 9 H, GeMe) and 7.46–7.83 (m, 5 H, aromatic); $\delta_C(CDCl_3)$ −1.2 (GeMe), 127.7–140.4 (aromatic) and 234.3 (CO).

S-Ethyl thiolbenzoate (*S-Ethyl benzenecarbothiolate*): λ_{max}(isooctane)/nm 266 (log ε = 3.86) and 236 (4.07).

Methyl benzenecarboselenoate.[27] M.p. and spectral data as ref. 28. λ_{max}(isooctane)/nm 297 (br, log ε = 3.48), 284 (3.57), 238 (4.09) and 204 (4.24); $\delta_C(CDCl_3)$ 194.6 (CO).

Butyl benzenecarbotelluroate.[29] λ_{max}(isooctane)/nm 346 (v br, log ε = 3.41), 290 (3.20), 280 (sh, 3.26), 244 (4.29) and 205 (4.35).

Benzoyl iodide. See ref. 30.

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