ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 4, pp. 710–713. © Pleiades Publishing, Ltd., 2011.
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Effect of the X and Y Substituents on the Carbonyl Bond in 4-$YC_6H_4C(O)X$ Compounds

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Received January 18, 2010

Abstract—Mechanistic aspects of the effect of the X and Y substituents (X = Me, H, CF_3, CN, Br, Cl, F, OH, NH_2; Y = H, NMe_2, NH_2, CN, NO_2) on the carbonyl bond in 4-$YC_6H_4C(O)X$ compounds are discussed on the basis of the ^{13}C and ^{17}O NMR data.

DOI: 10.1134/S1070363211040153

Electronic structure of carbonyl group in aromatic compounds is the subject of numerous studies [1, 2], including those performed on the basis of ^{13}C and ^{17}O NMR data [3, 4]. Studies on 4-$YC_6H_4C(O)X$ and PhC(O)X compounds, where X = Me, H, CF_3, CN, Br, Cl, F, OH, NH_2 and Y = H, NMe_2, NH_2, CN, NO_2, showed that the ^{13}C and ^{17}O chemical shifts are largely determined by the properties of the X substituent directly linked to the carbonyl group and the Y substituent in the aromatic ring. The nature of these dependences is the subject of the present study.

As shown previously [5], interaction between the Y and C(O)X substituents in aromatic compounds like 4-$YC_6H_4C(O)X$ is largely contributed by so-called "positive charge effect" (PCE). In keeping with the PCE concept, increase of the electronegativity (EN, χ) of the A atom within a narrow series of structurally similar compounds of the general formula ABC consisting of non-transition elements, where B is a positively charged atom, is accompanied by increase of the negative charge on the C atom in spite of the inductive effect of A. Thus, according to the PCE, increase of the EN of X in PhC(O)X leads to increase of the negative charge on the oxygen atom. The effect of the Y substituent on the carbonyl carbon and oxygen atoms in $YC_6H_4C(O)X$ may be interpreted as follows. Let us assume that the C^1 atom in the benzene ring (i.e., that bearing the carbonyl group) and the carbonyl carbon atom possess a positive charge. Electron-withdrawing substituent Y in the *para* position with respect to the C(O)X group increases the positive charge on C^1, which leads to charge transfer to the carbonyl carbon atom, and the positive charge on the latter decreases (the corresponding ^{13}C signal shifts upfield). On the other hand, the negative charge on the carbonyl oxygen atom decreases, and its NMR signal shifts downfield. Correspondingly, electron-donating substituent Y exerts the opposite effect: the positive charge on C^1 decreases the positive charge on the carbonyl carbon atom increases, and the negative charge on the carbonyl oxygen atom increases. The effect of Y on the charge on C^1 is determined by its inductive (σ_I) and mesomeric (σ_R) parameters [5, 6]. If the charge on C^1 is negative, interaction between Y and C(O)X in 4-$YC_6H_4C(O)X$ is determined by the electrophilicity of the C(O)X group (see below).

The electronic structure of some molecules was analyzed by *ab initio* quantum-chemical calculations (RHF/MP2/MINI-4//RHF/MP2/MINI-4) where scaling factors of valence atomic orbitals were optimized by energy minimization [7]. The experimental ^{13}C and ^{17}O NMR data were used. The chemical shifts of ^{17}O and ^{13}C are determined mainly by the paramagnetic constituent (σ^p) of the shielding constant. In terms of the Karplus–Pople approximation [8], the paramagnetic contribution is given be the equation

$$\sigma^p = -\text{const}\,\Delta E^{-1}\,r^{-3}\,\Sigma\,Q.$$

Here, ΔE^{-1} is the reciprocal averaged electronic excitation energy of a molecule under study, r^{-3} is the averaged reciprocal cubed radius of the 2*p* orbital of a given atom, and ΣQ is the bond order–charge density matrix. Structurally similar aromatic compounds are characterized by linear relations between $\delta^{13}C$ and electron density q on the carbon atom, calculated by quantum-chemical methods: $\delta^{13}C = Aq + B$, where A and B are constants [9, 10]. Variation of $\delta^{13}C$ reflects the tendency in variation of the charge on the carbon atom within a series of compounds. The term ΔE is usually assumed to be equal to the averaged energy of low-lying (n–π*) transitions in the UV spectra, and the term $\sum Q$ for carbonyl compounds is approximated by the π-order of the carbonyl bond (either calculated or determined on the basis of the ^{17}O NQR data). Cheng and Lin [11] showed that the π-order (P^{π}) of the carbonyl bond is the main factor determining the $\delta^{17}O$ value of carbonyl compounds PhC(O)X (X = H, Ph, F, Cl, OR, O^-). Some authors presumed that increase of electron density on the oxygen atom in such compounds leads to increased shielding of that atom [12]. The ^{13}C and ^{17}O chemical shifts (ppm) given below were determined relative to the compound with Y = H; negative values indicate upfield shift, and positive, downfield shift.

Let us consider interaction between the X substituent and carbonyl group in PhC(O)X. Here, the effect of X on the chemical shift of ^{17}O is significant: $\Delta\delta_O$ is equal to 218 ppm in going from X = F to X = I [11]. In this case, deshielding of the oxygen atom cannot be rationalized in terms of inductive effect of halogen atoms (it weakens in the series F > Cl > Br > I) or ΔE values (the energy of n–π* transition in these compounds is very small) [13]. Analysis of the ^{17}O NQR data for PhCOF and PhCOCl showed that the π-order of the C=O bond in benzoyl chloride is greater, which implies larger paramagnetic constituent of the shielding constant and downfield shift of the ^{17}O signal ingoing from benzoyl fluoride to benzoyl chloride [11]. Analogous variation of the order of the C=O bond follows from *ab initio* calculations. The calculation results also showed increase of the positive charge on the carbon atom and of the negative charge on the oxygen with rise of electronegativity of the halogen atom: PhCOCl: $P^{\pi} = 0.720$, $q_C = 0.3595$ a.u., $q_O = -0.3021$ a.u.; PhCOF: $P^{\pi} = 0.702$, $q_C = 0.5994$ a.u., $q_O = -0.3493$ a.u.

On the other hand, a satisfactory correlation exists between the ^{17}O chemical shifts of benzoyl halides and Pauling electronegativities of halogen atoms (X = F, Cl, Br) [11]:

$$\delta^{17}O = -(118 \pm 17)\chi + (825 \pm 53). \quad (1)$$

Analogous dependence is typical of the PCE: the larger the EN of the A atom in ABC compound, the greater the gain in the electron density on the C atom [14]. Presumably, PCE is the main factor determining the experimental data. The effect of lone electron pair (UEP) on halogen atoms cannot be significant, taking into account that halogens are weak π-donors as compared, e.g., to nitrogen and oxygen (interaction between halogen UEP and positively charged halogen nucleus is stronger). According to our calculations, the PCE is significant not only for π-order but also for σ-order of the C=O bond, and polarization of that bond increases in going from benzoyl chloride to benzoyl fluoride.

It should be noted that the ^{17}O chemical shifts of acetyl fluoride (δ_O 374 ppm), chloride (δ_O 502 ppm), and bromide (δ_O 536 ppm) differ from the corresponding values found for benzoyl halides by 19±5 ppm [11]. Presumably, the PCE is the main factor determining the ^{17}O chemical shift in both series of compounds.

The ^{17}O chemical shifts do not fit Eq. (1) when X = CF_3, CN, COOEt. In order to interpret the effect of these substituents on the carbonyl bond, the results of studying their interaction with a carbocationic center should be considered. In keeping with the experimental data reported in [15, 16], carbonyl and cyano groups destabilize cationic species to a lesser extent than that expected on the basis of their inductive parameters. Dixon et al. [17] performed a theoretical study and attributed weaker destabilizing effect to resonance effect which implies delocalization of the π-orbital of electron-withdrawing substituent over the vacant orbital of the carbocationic center. The same may be rationalized as follows in terms of the PCE. Successive replacement of hydrogen atoms in the methyl group in PhC(O)Me molecule by fluorine atoms is accompanied by increase of electronegativity in the series $CH_2F < CHF_2 < CF_3$ and increase of the positive charge on the corresponding carbon atom. Simultaneously, charge transfer from the carbonyl carbon atom to CF_nH_{3-n} increases, while increase in the positive charge on the carbon atom (in keeping with PCE) induces charge transfer (including π-charge transfer) in the opposite direction, from the CF_3 group to the carbonyl carbon atom. As a result, destabilization of the carbonyl group becomes weaker, and the effective EN of the trifluoromethyl group decreases. Here, electron density deficit in the C=O group is necessary. Analogous pattern is intrinsic to compounds in which the first atom in the X group is a positively charged atom linked to electronegative atoms, e.g., X = C≡N or C≡CH.

Relative ^{13}C and ^{17}O chemical shifts (ppm) in the NMR spectra of 4-$YC_6H_4C(O)X$ compounds

Y	X = Me		X = H		X = NH_2		X = OH	
	$\delta^{13}C$	$\delta^{17}O$	$\delta^{13}C$	$\delta^{17}O$	$\delta^{13}C$	$\delta^{17}O$	$\delta^{13}C$	$\delta^{17}O$
NMe_2	–1.70	–	–2.19	–41.4	0.05	–9.4	0.16	–
NH_2	–1.60	–39.0	–1.88		0.15	–10.7	0.23	
H	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0

Likewise, Eq. (1) is inapplicable to ^{17}O chemical shifts in compounds with X = OH, NH_2. Presumably, the effect of these substituents on $\delta^{17}O$ is determined by two factors: (1) interaction between UEP on the oxygen or nitrogen atom in OH or NH_2 group and the carbonyl carbon atom and (2) PCE. Hydroxy group is characterized by a fairly strong electronegativity (χ = 3.5), whereas small effective EN of amino group (χ = 3.0) is compensated by its strong +R-effect [18]. As a result, the calculated π-order of the C=O bond in PhC(O)X molecules decreases ingoing from benzaldehyde (X = H) to benzoic acid (X = OH) and benzamide (X = NH_2), and the oxygen atom becomes more shielded: PhC(O)H: $P^{\pi} = 0.738$; PhC(O)NH_2: $P^{\pi} = 0.650$, q_C = 0.5197 a.u., q_O = –0.4812 a.u.; PhC(O)OH: $P^{\pi} = 0.659$, q_C = 0.5471 a.u., q_O = –0.5788 a.u. Analogous results were obtained by calculation of MeC(O)OH and MeC(O)NH_2 molecules [19].

Interaction between the Y and C(O)X substituents in 4-$YC_6N_4C(O)X$ molecules is discussed below. According to an empirical rule, the effect of Y on C(O)X is determined by electrophilicity (or electron deficit) of the latter, i.e., it depends on the nature of X to a considerable extent: the lower the electron-donating power of X, the larger the electron deficiency of the carbonyl group and the stronger the effect of Y on $\delta^{17}O$ [20]. In keeping with the reactivity of the corresponding compounds, the electrophilicity of the C(O)X groups increases in the following series: $COO^- < CONH_2 < COMe < COCF_3$ [21]. The quantity $\rho^+ = \delta(^{17}O)/\sigma^+$, where σ^+ is the Hammett–Taft parameters, was also proposed as a measure of electrophilicity. The electrophilicity of C(O)X increases as ρ^+ rises: C(O)OH, 7.3; C(O)NH_2, 7.3; C(O)F, 14.1; C(O)Me, 22.5; C(O)H, 26.3; C(O)CF_3, 29.0 [20]. More electrophilic groups [C(O)Me, C(O)H, C(O)CF_3] are characterized by larger difference in the ^{17}O chemical shifts ($\Delta\delta^{17}O$) for donor and acceptor substituents Y, as compared to less electrophilic groups [C(O)OH, C(O)NH_2]. For instance, the $\Delta\delta^{17}O$ values for C(O)Me (Y = NH_2, NO_2), C(O)CF_3 (Y = NMe_2, CN), and C(O)NH_2 (Y = NMe_2, NO_2) are 56.0, 61.4, and 15.3 ppm, respectively [20]. The effect of the substituent Y on the C(O)X group in such compounds is determined by the sign of the charge on C^1 in PhC(O)X. This charge can also be estimated from the ENs of the phenyl and C(O)X groups by quantum-chemical calculations. For example, χ_{Ph} = 2.7–2.8, $\chi_{C(O)H}$ = 2.8, $\chi_{C(O)OH}$ = 2.9–3.15, $\chi_{C(O)NH2}$ = 3.0 [18, 22]. According to the results of CNDO/2 calculations, the charges on C^1 in PhC(O)H, PhC(O)Me, and PhC(O)OH are fairly small and negative, q_C1 = –0.016, –0.020, and –0.035 a.u., respectively [23]. The calculations performed in the present work for the first two compounds gave fairly similar results, while q_{C^1} = 0.019 a.u. for PhC(O)OH and q_C = 1 0.015 a.u. for PhC(O)NH_2 were obtained. Presumably, the charge on C^1 in PhC(O)H and PhC(O)Me is negative, and that in PhC(O)OH and PhC(O)NH_2 is positive; the same follows from comparison of the ENs of the phenyl and C(O)OH and C(O)NH_2 groups. The above assumptions make it possible to rationalize the ^{13}C and ^{17}O chemical shifts in the NMR spectra of 4-$YC_6H_4C(O)H$ and 4-$YC_6H_4C(O)NH_2$ (see table) [20, 24].

Introduction of electron-donating substituents Y (Y = NH_2, NMe_2) into PhC(O)Me and PhC(O)H molecules increases the negative charge on C^1. In this case, interaction between the benzene ring and C(O)X group is determined by the inductive effect (electrophilicity) of the C(O)X group, which simultaneously increases shielding of the carbonyl carbon and oxygen atoms. More electrophilic (electron-deficient) C(O)X groups are characterized by stronger shielding of the oxygen atom and hence larger difference between the ^{17}O chemical shifts for typical donor and acceptor groups Y.

Electron-withdrawing substituents Y (CN, NO_2) which generally exert a considerable inductive effect are likely to change the negative charge on C^1 to positive. In keeping with the PCE, shielding of the carbonyl carbon atom increases, and the carbonyl oxygen atom becomes deshielded. For example, 4-$Me_2NC_6H_4C(O)H$ is characterized by the following chemical shifts: $\delta^{13}C$ –2.12, $\delta^{17}O$ –41.4 ppm [hereinafter, relative to PhC(O)H; negative values indicate upfield shift]; 4-$NO_2C_6H_4C(O)NH_2$: $\delta^{13}C$ –1.75, $\delta^{17}O$ 17.0 ppm.

The chemical shifts of the carbonyl carbon and oxygen atoms in $YC_6H_4C(O)X$ (X = NH_2, OH) change as follows: electron-donating substituents induce deshielding of the carbonyl carbon atom and shielding of the oxygen atom; the opposite pattern is observed for electron-withdrawing substituents, i.e., the chemical shifts change according to the PCE: 4-$Me_2NC_6H_4C(O)NH_2$: $\delta^{13}C$ 0.05, $\delta^{17}O$ –9.4 ppm; 4-$O_2NC_6H_4C(O)NH_2$: $\delta^{13}C$ –1.65, $\delta^{17}O$ 7.8 ppm [relative to $PhC(O)NH_2$].

Apart from the direct effect on the electrophilicity of the carbonyl group, the X group also affects the charge on C^1. The charge on C^1 in the most electrophilic benzoyl compound $C_6H_5C(O)^+$ was estimated at $q_{C^1} = -0.2262$ a.u. (calculations performed in the present work). This charge is so large that it cannot change its sign by the action of acceptor substituent Y, while donor substituent Y increases it even more strongly. In this case, the ^{13}C NMR spectrum displays normal [5] (rather than anomalous reverse [24]) variation of the chemical shift of the carbonyl carbon atom, depending on the nature of Y: donor substituents Y induce upfield shift the carbon signal, and acceptor substituents, downfield shift [25].

Thus the effect of the Y substituent on the carbonyl bond in $YC_6H_4C(O)X$ compounds is determined by the sign of the charge on C^1, which depends in turn on the electrophilicity of the C(O)X group, i.e., on the nature of X.

Quantum-chemical calculations were performed using GAMESS program [26].

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