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Relationship between Electron Densities and Chemical Shifts.† 3. Para-Substituted Benzoyl Cations

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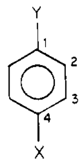
Abstract: Ab initio molecular orbital calculations have been made for a series of para-substituted benzoyl cations, $X–C_6H_4–CO^+$, where X = NH_2, OH, F, CH_3, H, CF_3, CN, NO_2. Substituent-induced changes in π electron densities at the C-1 position (para to X and adjacent to the $C^+{=}O$ group) follow the expected trends. Resonance-donating substituents increase the π electron density and acceptors reduce it. These trends compare closely with available ^{13}C substituent chemical shift (SCS) data for this position. However, for the side-chain C-α position, although a reasonable correlation between SCS data and π electron densities is obtained, the slope is not in the expected direction. The SCS data indicate a "reverse" substituent effect at this position, while the calculations predict a "normal" direction. A number of proposals to rationalize this trend are discussed.

In recent reports[1-6] we have examined relationships between ^{13}C and ^{19}F substituent chemical shifts (SCS) and electron densities in the side chains of aromatic derivatives. Reasonable correlations between these terms are found for series having the general structure shown below (**1**) where the fixed side chain (Y) containing the probe site is well separated from the variable substituent (X).



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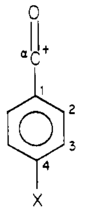

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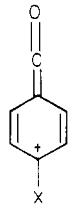
From studies of ring and side-chain positions in neutral substituted benzenes,[1-8] it is found that, in general, π components of electron densities provide a more satisfactory correlation with ^{13}C and ^{19}F SCS values than do σ or total components. To gain a greater understanding of the features controlling ^{13}C substituent chemical shifts, it is necessary to extend these studies to charged systems. In 1975, Larsen and Bouis[9] presented a communication in which they pointed out some apparent anomalies with regard to the correlation of CNDO/2 charge densities and ^{13}C chemical shifts[10] in para-substituted benzoyl cations (**2**). In their communication, they suggested that more sophisticated calculations might resolve some of these anomalies. This paper fulfills that need and corrects some of the conclusions made by Larsen and Bouis.[9]

Results and Discussion

Electron densities, calculated at the ab initio (STO-3G) level of theory for a range of substituted benzoyl cations, are given in Table I. The data are expressed relative to the parent (unsubstituted) compound to give a clear picture of substituent effects in this series. π electron densities for the C-1 position (para to the changing substituent) follow the expected trend in that donating substituents bring about an increase in π electron density and acceptors a decrease. This trend is paralleled in the ^{13}C SCS data (i.e., the increased π electron density for donors is associated with an upfield shift). Figure 1 shows the satisfactory correlation between the two quantities (the magnitude of the slope is 353 ppm/electron; r = 0.976). Unfortunately, the number of data points is limited because of the experimental difficulties associated with obtaining SCS data for substituents such as CN and NO_2. (Under the acid conditions necessary to generate the benzoyl cations, these substituents are themselves protonated, to produce substituent groups with markedly different electronic properties.) However, in spite of the limited data set, it is clear that no unusual direction of substituent effect is seen for the C-1 position.

This is in contrast to an interpretation made by Larsen and Bouis,[9] who suggested that their assumed anomalous direction of C-1 SCS effects had earlier been rationalized (by Olah and Westerman[10]) by contributions from "ketene-like" resonance forms (**3**). In fact, Olah and Westerman[10] did discuss ketene-like forms and provided convincing arguments for their existence, as have other authors.[11] However, they did not use these contributions to rationalize an anomalous SCS direction at the C-1 position. *No such anomalous effect exists.*



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Since we have established that π electron densities at C-1 follow the expected trends, it is now relevant to note that total electron densities also correlate well with the SCS values. The magnitude of the slope (867 ppm/electron, r = 0.994) is somewhat larger than for the corresponding relationship with π electron densities, reflecting the smaller range in total electron densities. Total electron densities are simply the sum of the σ and π components, and, at the C-1 position in benzoyl cations, we find that there is a precise linear relationship between these individual components (eq 1). The precise nature of this relationship implies that σ

$$\Delta q_\sigma = -0.53\Delta q_\pi \qquad (r = 0.999) \qquad (1)$$

electron densities also correlate well with observed SCS values. However, unlike the π and total components, trends in σ electron densities have the wrong sign to account for the observed SCS trend. Nevertheless, the σ–π relationship itself is of inherent interest, as in other series the existence of such relationships has been attributed[7] to a repulsion of σ electron density resulting from

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† For Parts 1 and 2 see ref 1 and 2.

(1) Brownlee, R. T. C.; Craik, D. J. *Org. Magn. Reson.* **1980**, *14*, 186.

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Table I. Substituent-Induced Changes in Electron Densities in Para-Substituted Benzoyl Cations[a]

	C-1			C-α			oxygen			C-1[b]	C-α[b]
X	σ	π	total	σ	π	total	σ	π	total	SCS	SCS
NH_2 (pl)[c]	−225	408	182	42	199	241	−107	320	213		
NH_2 (py)[d]	−188	334	146	22	152	174	−76	253	177		
NH_2 (t)[e]	−176	316	139	26	141	167	−78	233	155		
OH	−170	291	122	18	111	129	−76	189	113	−10.6	6.6
F	−99	157	59	2	45	47	−53	77	25	−4.3	−0.2
CH_3	−57	110	54	10	42	52	−12	86	74	−4.9	1.7
H	0	0	0	0	0	0	0	0	0	0.0	0.0
CF_3	24	−57	−33	−17	−16	−33	−1	−52	−53		
CN	33	−86	−54	−34	−11	−45	−7	−70	−77		
NO_2	78	−173	−95	−46	−40	−86	−4	−146	−150		
CO^+										20.7	−9.6
$C_6H_5CO^+$[f]	4.8351	1.2061	6.0412	4.7347	0.7743	5.5090	6.5683	1.4405	8.0088		
C_6H_5COF[g]	4.9926	1.0438	6.0364	4.7408	0.9348	5.6756	7.0514	1.1939	8.2453		

[a] Electron densities expressed relative to the H substituent $\times 10^4$; a positive value represents an increase in electron density. [b] SCS data (ppm) from ref 10 for substituted benzoyl cations; a positive value represents a downfield shift. The chemical shift for the OH substituent is that for OMe, which has very similar substituent properties. [c] Planar amino geometry. [d] Pyramidal amino geometry. [e] Tetrahedral amino geometry. [f] Absolute electron densities in the benzoyl cation. [g] Absolute electron density in benzoyl fluoride.

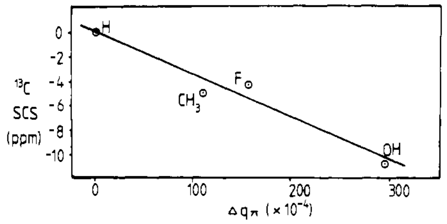

Figure 1. Plot of ^{13}C SCS values vs. π electron densities for C-1 in *p*-X-benzoyl cations.

a local buildup in π electron density. The slope of eq 1 is slightly smaller in magnitude than the corresponding σ–π relationship in monosubstituted benzenes (where $\Delta q_\sigma = -0.57\Delta q_\pi$),[12] reflecting a decreasing response of the σ framework to changes in π electron density. The electronegative nature of the $C^+{=}O$ group apparently reduces the polarizability of the σ-framework.

The data for the C-α position are more difficult to interpret. Larsen and Bouis[9] noted that no correlation was obtained between SCS values and Hammett substituent constants at this position. This observation does not necessarily mean that the SCS values are not systematically dependent on electronic substituent parameters. It is now well documented[13,14] that single-parameter Hammett-type analyses of SCS data are often inadequate, because the blend of polar and resonance contributions may vary at different measuring sites. The dual substituent parameter (DSP) method[13] overcomes this disadvantage. Equation 2 shows that

$$\mathrm{SCS} = \rho_I\sigma_I + \rho_R\bar{\sigma}_R \qquad (2)$$

in this method, the property being examined is correlated with a linear combination of the two substituent constants, σ_I and $\bar{\sigma}_R$, where $\bar{\sigma}_R$ may be any one of σ_R^-, σ_R^0, σ_R^{BA}, or σ_R^+, depending on the electron demand placed on the substituent by the measuring site.

While it would be desirable to apply the DSP method to the SCS data for the C-α position in the benzoyl cations, unfortunately it is not realistic to do so. This is because in order to obtain a reliable separation of polar and resonance effects, a basis set of substituents is required.[13] As we noted earlier, the experimental conditions under which the SCS data in Table I were obtained preclude the determination of SCS values for many of the additional substituents required to complete a basis set. Although a detailed DSP analysis is not possible, a qualitative examination of the ^{13}C SCS data for the C-α position shows that a reverse direction occurs and that polar and resonance effects both make important contributions. The reverse effect may be seen by noting that the resonance-*donating* substituents OMe and Me cause *downfield* shifts while the electron-withdrawing substituent CO^+ causes an upfield shift of the C-α resonance. The datum for the fluoro substituent illustrates the reverse contribution from both polar and resonance effects. The relatively small SCS value for this substituent arises because it has a large σ_I value, which is of opposite sign to its σ_R value.

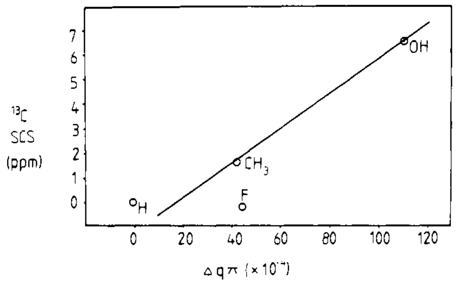

Figure 2. Plot of ^{13}C SCS values vs. π electron densities for C-α in *p*-X-benzoyl cations.

A semiquantitative estimate of the relative importance of polar and resonance effects may be obtained from a graphical representation of the DSP equation,[14] rearranged to the form of eq 3,

$$\mathrm{SCS} = (\rho_I^2 + \rho_R^2)^{1/2}(\sigma_I \cos\theta + \sigma_R \sin\theta) \qquad (3)$$

where each SCS value is factored into the product of an effective ρ value ($\bar{\rho} = (\rho_I^2 + \rho_R^2)^{1/2}$) and an effective σ value ($\bar{\sigma} = \sigma_I \cos\theta + \sigma_R \sin\theta$) where $\tan\theta = \rho_R/\rho_I = \lambda$.

From a plot[14] of the effective σ value, $\bar{\sigma}$, vs. θ we determine that the general ordering of the C-α SCS values for the OMe, F, Me, and H substituents corresponds to a θ value in the range 50–60°. This is equivalent to a λ value of about +1.5 and shows that the ^{13}C shifts at this position reflect a slightly larger relative contribution from resonance effects than polar effects. However, the point of major importance is that the derived λ value is positive, showing that the polar and resonance transmission coefficients are of the same sign. Both effects are in a reverse direction.

In contrast to the SCS values, the π electron densities at C-α indicate a normal direction of substituent effects. Donors such as NH_2 and OMe increase the π electron density at this site, and acceptors such as CF_3 and NO_2 decrease it. The Δq_π values fit the DSP equation with good precision ($f < 0.1$), indicating that they are systematically related to substituent σ_I and σ_R^+ values (eq 4).

$$10^2\Delta q_\pi = -0.4\sigma_I - 1.2\sigma_R^+ \qquad (f = 0.08) \qquad (4)$$

Figure 2 shows that a qualitative relationship exists between the π electron densities and chemical shifts, but the slope has the opposite sign to that for the C-1 position in Figure 1. At this stage

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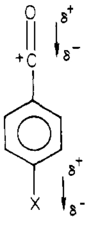
it is difficult to determine whether this is due to anomalous SCS values or anomalous electron densities, as reasonable arguments can be proposed to support the direction of substituent effects predicted by either the calculations or the NMR data. For example, the reverse effect indicated by the SCS data is indicative of a π-polarization mechanism[3,4,15] involving the through-space polarization of the C=O π system by the substituent dipole as shown in **4**.



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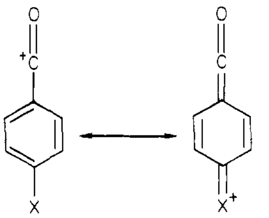
This mechanism has been used to explain ^{13}C SCS values in a number of neutral carbonyl series,[3,4] as well as in other series containing π systems capable of undergoing polarization by a remote substituent.[15,16] The carbonyl π system in **4** is aligned favorably with the substituent dipole so that electron-attracting groups, X, can polarize the C=O bond, increase the electron density at C-α, and reduce it at the terminal oxygen atom. The shielding (resulting from the increased electron density) at C-α produced by the electron-attracting substituent would account for the reverse SCS direction. The fact that the theoretically derived π electron densities do not support the polarization pattern implied by the SCS data suggests that the calculations might not accurately describe the electron distribution in the charged side chain. One possibility is that the calculations overestimate the importance of resonance structure **2**. Here, the positively charged nature of the C-α site means that it is able to directly conjugate with the substituent, as shown in **5**.



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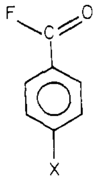
This substituent effect is in a normal direction, as the *donor* X brings about an *increase* in π electron density on the C-α atom proportional to the σ_R^+ value of X. This mechanism accounts for the resonance contribution to Δq_π ($\rho_R = -1.2$) seen in eq 4 although the effect is opposite in sign to that predicted by the SCS data. Equation 4 also shows that the calculations provide no evidence of a reverse polar effect at C-α arising from localized π polarization of the C=O bond. It should be stressed that the apparent failure of the calculations to predict the direction of SCS values for the C-α position in this series is not due to a *general* inadequacy of the theory, because in many series the theoretical results do support the π-polarization concept. For example, in benzoyl fluorides (**6**) (percursors of the benzoyl cations), ab initio calculations predict an increase in π electron density at C-α for electron-withdrawing dipolar substituents.[6]



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The calculated π electron densities at C-α in series (**6**) correspond closely with the observed reverse ^{13}C SCS direction at this position.[1,3,6] The theoretically predicted reverse polar effect is shown by the opposite sign of the ρ_I value in eq 5 (for the benzoyl fluorides),[6] compared to that in eq 4 (for the benzoyl cations).

$$10^2\Delta q_\pi = +0.7\sigma_I + 1.0\sigma_R^0 \qquad (f = 0.17) \qquad (5)$$

A comparison of the theoretical results for the two series therefore suggests that localized C=O polarization is reduced in the benzoyl cations, most likely a result of significant contributions from ketene-like structures such as **3**. Previous experimental[10] and theoretical[17] studies support this view. An increasing contribution from this type of structure reduces the effects of π-polarization of the C=O bond since the adjacent C-1—C-α bond can also be polarized. Further, in benzoyl cations, substituent-induced polarization of the C-O bond is expected to be smaller than in neutral carbonyl series like **6** because of an increased C=O π bond polarity in the former case. The C-α and oxygen π electron densities in benzoyl cation and benzoyl fluoride given in Table I show that the larger inherent polarity (as measured by the difference in π electron densities between the C-α and oxygen atoms) of the π bond in the former series makes it less susceptible to polarization by the distant substituent X; i.e., the bond polarity is increased but its polarizability is reduced.

Another factor which must be taken into account is that the C-α SCS data may be strongly influenced by solvent effects. The calculations represent theoretical substituent electronic effects in the absence of intermolecular interactions. Most recent studies[1-3,6,15,16] of the effects of ring substituents on ^{13}C shifts at side-chain carbon atoms of aromatic series rely on the measurements being made in dilute solutions of an inert solvent; however, the SCS data in Table I were not recorded under these conditions,[10] and it is likely that solvation of the positively charged side chain and intermolecular effects are very important. For example, the resonance structure Ph—C≡O$^+$ may be stabilized in superacid relative to the gas phase. The effect of such solvation has not been included in the calculations presented here. On the other hand, the C-1 shifts follow a more predictable trend because this site is protected within the molecular framework and hence is less susceptible to external effects.

Conclusions

The effects of substituents on the C-1 ring-carbon shifts in para-substituted benzoyl cations are readily explained in terms of changes in π electron densities at this site. On the other hand, the shifts at the C-α position are in a direction opposite to that predicted by π (or σ or total) electron densities.

Computational Details

The calculations were done by using a modified version of the GAUSSIAN 70 series of programs,[18] using the STO-3G basis set. The bond lengths used for C-1–C-α and C-α–O were 1.387 and 1.111 Å, respectively. These were the values previously used by Larsen and Bouis[9] in their CNDO/2 calculations and had previously been obtained from X-ray data.[11] Standard geometries were assumed for the ring[7] and substituent fragments[19] of the molecules examined. The OH group was used as an approximation for OCH_3. Three different geometries for the amino substituent were calculated because of the uncertainty regarding the amino geometry in different aromatic systems.[20] These geometries correspond to a planar, tetrahedral, and pyramidal[21] arrangement of

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bonds about the central nitrogen atom. Because of the general tendency of increased planarity of the amino group in the presence of para electron-withdrawing substituents,[20] the planar geometry is most appropriate in the benzoyl cations.

Acknowledgment. We thank the La Trobe University Computer Centre for a generous allocation of computer time and facilities. D.C. gratefully acknowledges support in part from a CSIRO postdoctoral studentship and a Monash postdoctoral fellowship.

Registry No. 2 ($X = NH_2$), 84132-25-2; **2** (X = OH), 56176-50-2; **2** (X = F), 39981-36-7; **2** ($X = CH_3$), 20122-40-1; **2** (X = H), 19270-10-1; **2** ($X = CF_3$), 46061-29-4; **2** (X = CN), 56176-49-9; **2** ($X = NO_2$), 45945-94-6.

Cyclization of 3-(Arylchalcogeno)propenoyl Chlorides. 1. 1,2-Oxatellurol-1-ium Halides via "Ipso" Acylation

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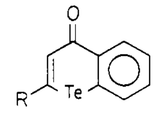
Abstract: 3-(Aryltelluro)propenoyl chlorides react thermally and with Lewis acids to give products of rearrangement that are identified as new tellurium heterocycles, 1,2-oxatellurol-1-ium chlorides. The heterocyclic nature of the compounds was confirmed by single-crystal X-ray crystallography, which also showed a chlorine–tellurium bond with a nearly linear (170°) Cl–Te–O array containing fractional bonds. A bonding picture utilizing a three-center, four-electron bond is described. ^{125}Te NMR spectroscopy suggests that Te(IV) may be the correct oxidation state for tellurium in these compounds. The chlorine in these molecules is easily exchanged for other halogens as well as trifluoroacetate. The rearrangement appears to involve "ipso" acylation followed by aryl migration to give the observed products. The rates of rearrangement, both thermal and Lewis acid catalyzed, are sensitive to substituent effects.

Interest in the preparation of tellurium analogues of various heterocyclic systems has been increasing. Two systems that have been successfully prepared are tellurochromones (**1**)[1] and telluroxanthone (**2**).[2] Although the cyclizations of β-(arylthio)- and β-(arylseleno)acrylic acids (**3**) have been useful for the preparation of 4*H*-(benzo[*b*]thio)pyrones and 4*H*-(benzo[*b*]seleno)pyrones,[3] the extension of the reaction to include the cyclization of β-(aryltelluro)acrylic acids and derivatives has not been described.



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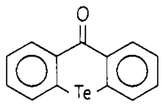

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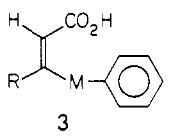

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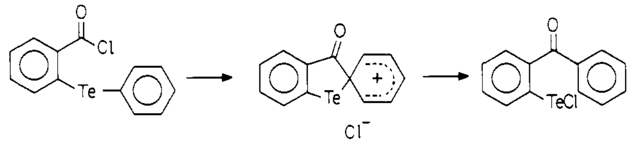
M = S, Se, Te

The reaction of *o*-(phenyltelluro)benzoyl chloride (**4**) with zinc chloride has been reported to give not **2** but a rearrangement product, *o*-(chlorotellurenyl)benzophenone (**5**).[4] This product presumably arises by attack of an acylium species or its equivalent on the carbon bearing tellurium to give a spirocyclic intermediate followed by fission of the carbon–tellurium bond to give an aryl migration and the observed product.[4,5]



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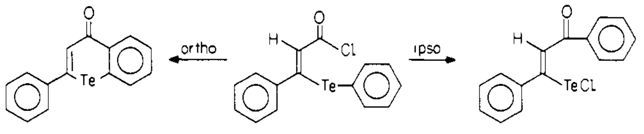
The rearrangement product **5** displayed some interesting spectral features.[4] The IR carbonyl stretching frequency was 1580 cm^{-1}. This lowering of the stretching frequency was attributed to an interaction between the carbonyl oxygen and the tellurium atom.

Scheme I



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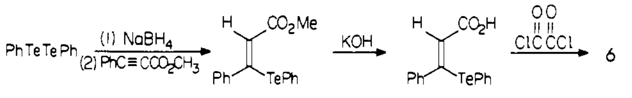
Scheme II



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We were interested in the fate of β-(aryltelluro)acryloyl and -cinnamoyl chlorides when treated with Lewis acids. The questions of whether ortho or ipso acylation would predominate and what would be the properties of the products were of particular interest. Herein, we report the Lewis acid and thermally induced rearrangements of β-(aryltelluro)acryloyl and -cinnamoyl chlorides, which proceed by ipso acylation. The rearrangement products show strong tellurium–oxygen interactions and represent a new class of tellurium heterocycles, 1,2-oxatellurol-1-ium chlorides.

Results and Discussion

Although tellurochromones have been prepared (**1**, R = H, CH_3),[1] telluroflavones (**1**, R = Ph) have yet to be described. With this fact in mind, we first examined the reaction of β-(phenyltelluro)cinnamoyl chloride (**6**) with aluminum chloride. If ortho acylation were observed, telluroflavone (**7**) would be the expected product, whereas ipso acylation should lead to the vinyltellurenyl chloride **8** (Scheme I).

The synthesis of **6** was straightforward, as indicated in Scheme II. The reduction of diphenyl ditelluride with sodium borohydride in ethanolic tetrahydrofuran (THF) gave a colorless solution of sodium phenyltelluride.[6] Methyl phenylpropionate was then

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