

Structural effects of carbon monoxide coordination to carbon centers. π and σ bindings in aliphatic acyl *versus* aromatic aroyl cations

Milya G. Davlieva, Sergey V. Lindeman, Ivan S. Neretin and Jay K. Kochi

Department of Chemistry, University of Houston, Houston, TX 77204-5003 USA

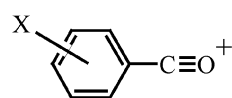
Received (in Montpellier, France) 19th May 2004, Accepted 14th September 2004

First published as an Advance Article on the web 16th November 2004

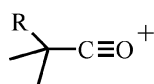
The binding of carbon monoxide to carbon centers has been examined with two series of aromatic and aliphatic oxocarbenium ions that are successfully isolated as crystalline and highly reactive (hygroscopic) aroylium and acylium salts with poorly coordinating counteranions. X-Ray crystallographic analyses at $-150\text{ }^{\circ}\text{C}$ afford precise structural parameters for the characteristic linear carbonyl bond (r_{CO}) and the bond to the carbon centers ($r_{\text{C}\alpha}$). The correlations of these structural parameters evaluated for alkyl (Me, Et and *i*-Pr) and aryl (*p*-Me, 2,4,6-trimethyl, *p*-MeO and *p*-fluorophenyl) oxocarbenium ions with the corresponding carbonyl stretching frequencies in the solid-state (reflectance) IR spectra yield valuable insight into the binding mode of carbon monoxide. Most noteworthy is the synergic (π - σ) bonding in aroylium structures in contrast to the mainly σ bonding in acylium structures that are organic mimics for carbon monoxide bonding in classical and nonclassical metal carbonyls, respectively.

Introduction

Owing to the relevance of carbon monoxide to a wide variety of metal-catalyzed processes of industrial importance, including hydroformylation, Fischer-Tropsch, carboxylation, *etc.* various types of metal carbonyls $\text{M}(\text{CO})_x$ have been isolated, synthesized and characterized as critical intermediates. Bonding among different metal carbonyls, especially of the transition series, is dominated by the classical model of synergic (σ - π) interactions of the CO base with different M-centered acids.¹ Recently, a different type of metal-carbonyl binding in which the usual π backbonding component is weak or nonexistent has been proposed for a new series of “nonclassical” metal carbonyls (the primary acid-base interaction deriving from a dominant metal σ orbital).² However, in metal-carbonyl bindings, the relative contributions of the σ and π components are difficult to assess quantitatively owing to the varying nature of the metal centers. It is thus noteworthy that there are a few examples from the organic literature in which CO is directly bonded only to carbon centers in the form of oxocarbenium moieties³ of two basic types, that is, (A) aromatic aroyl,⁴ and (B) aliphatic acyl cations.⁵ The first member of the aromatic class is the benzoyl cation ($\text{C}_6\text{H}_5\text{-C}\equiv\text{O}^+$) that allows direct π backbonding of the benzenoid ring to the σ -bonded CO substituent. Likewise, the first member of the aliphatic class is acetyl cation ($\text{CH}_3\text{-C}\equiv\text{O}^+$), in which the dominant σ bond allows little or no possibility of direct π conjugation. Importantly, both of these organic cations permit the effects of small (electronic) perturbations to be systematically examined by: (A) judicious placement of substituent groups on the phenyl ring, and (B) α branching at the methyl group, as depicted below:



(A) aroylium



(B) acylium

Acetyl cation was first isolated by Olah *et al.*³ in their now classic studies on the reactive intermediates in Friedel-Crafts acylations, and the X-ray crystallographic analysis of their colorless crystals was later reported by Boer.⁵ The corresponding X-ray structure of benzoyl cation is unreported, but the close analogs, the *o*- and *p*-methyl derivatives, were successfully examined by Le Carpentier, Weiss *et al.*⁴ In both cases, diffraction data were only collected at room temperature. The resulting limited precision (accuracy) of 1–1.5 pm (e.s.d.) did allow the overall structure elucidation, but was clearly insufficient for any quantitative or comparative conclusions to be drawn among various structural types. Accordingly in this study, we minimized such imprecisions (arising largely from thermal motion) by the low temperature re-examination of these structures, together with preparation of a new (extended) series of other aroylium and acylium salts.

Results

Isolation and crystallization of pure aroylium and acylium salts suitable for X-ray crystallography posed serious experimental difficulties for two principal reasons. First, as cationic salts, the choice of the appropriate (complex) counteranion for solubility in anhydrous solvents was critical, and an anion suitable for a given oxocarbenium salt was not predictably applicable to a close relative. Second, all oxocarbenium salts were sensitive to traces of moisture in the solvent and glassware, being extremely hygroscopic.⁶ For these reasons, the entries in the following tables were largely dictated by what we were successfully able to isolate; but we believe their number and variety were sufficient to establish the unique structural patterns of π and σ bonding relevant to aromatic *versus* aliphatic oxocarbenium structures as follows.

I. Synthesis and isolation of oxocarbenium salts

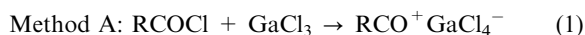
Two synthetic methodologies were utilized in the preparation of crystalline oxocarbenium salts suitable for X-ray crystallography. The more direct approach (Method A) was based on

Table 1 Geometric and IR parameters of aliphatic acyl cations^a

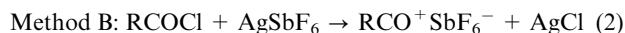
Cation	X [−]	<i>a</i> /Å	<i>b</i> /Å	α/deg	ν(CO)/cm ^{−1}	Source (Method)
Me-C≡O ⁺	SbF ₆ [−]	1.108(4) 1.11	1.419(4) 1.39	179.2(3) 177	2302 2294Ref. 3	This work (A) Ref. 5
Et-C≡O ⁺	GaCl ₄ [−]	1.102(5) 1.07	1.424(6) 1.43	178.6(5) 177	2282 —	This work (A) Ref. 8b
<i>i</i> -Pr-C≡O ⁺	SbCl ₆ [−]	1.101(4) 1.12	1.458(4) 1.44	177.4(3) 176	2257 Ref. 2 —	Ref. 2 Ref. 8b

^a Reliable data used for the discussion are given in bold.

Lewis acids such as antimony pentachloride and gallium trichloride applicable to Friedel–Crafts acylation with acid chlorides,³



in dichloromethane solution to generate the coordinatively saturated and low nucleophilic counteranions SbCl₆[−] and GaCl₄[−], respectively. The second method (Method B) was also found in Olah's earlier studies,³ and employed silver(I):



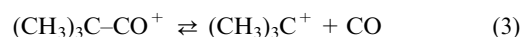
This method depended on the careful separation of silver chloride even as a trace contaminant that could otherwise inhibit crystallization. Methods A and B were used interchangeably because optimum conditions for successful crystallinity and solubility were largely a matter of trial and error among numerous attempts.

II. X-Ray crystallography of pure oxocarbonium salts

In order to quantitatively evaluate electronic effects on structure, the X-ray crystallographic analyses of the various acylium and aroylium salts were consistently carried out at −150 °C to a uniform precision of (e.s.d) 0.3–0.5 pm. In each case, the X-ray structural data were supplemented by infrared (reflectance) analyses of the carbonyl stretching frequency (ν_{CO}) in crystalline samples, as follows.

A. Aliphatic acyl cations. The low-temperature re-determination of the crystal structure of the acetyl salt CH₃–C≡O⁺SbF₆[−] (earlier thought to be disordered²) yielded the

structural parameters in Table 1 with good precision.⁷ We were also able to improve the earlier (imprecise) data⁸ on the structure of Et–C≡O⁺GaCl₄[−], which together with the recent (low-temperature) determination² of *i*-Pr–C≡O⁺SbCl₆[−] provided us with systematic observations on structure and electronic features of the aliphatic acyl cations in Table 1. Extension of the series to the highly branched pivaloyl cation was precluded owing to the reversible ready loss of carbon monoxide:⁹



The ORTEP diagram of the ethyl derivative Et–CO⁺GaCl₄[−] in Fig. 1(A) shows the linear coordination of CO in the basic 3 atom fragment C_α–C–O; and the (distorted) tetragonal disposition of chlorine from three GaCl₄[−] anions about the cationic center (*r*_{C...Cl} 3.28–3.48 Å) is identified by the unit-cell fragment in Fig. 1(B).¹⁰ Table 1 also includes the carbonyl stretching frequencies (last column) obtained from IR reflectance measurements on crystalline oxocarbonium salts (see Experimental).

B. Aromatic aroyl cations. Since our initial attempts to obtain single crystals of benzoylium salts with various counteranions suffered badly from low solubilities, we re-determined the structure of the methyl derivative *p*-CH₃C₆H₄–CO⁺SbCl₆[−] at −150 °C with superior resolution to that earlier reported by Le Carpentier, Weiss *et al.*⁴ In addition, the structural parameters are reported in Table 2 for the 2,4,6-trimethyl (Mes) and 2,3,4,5,6-pentamethyl (Me₅C₆) derivatives together with those of the *p*-fluoro- and *p*-methoxy-substituted analogs.

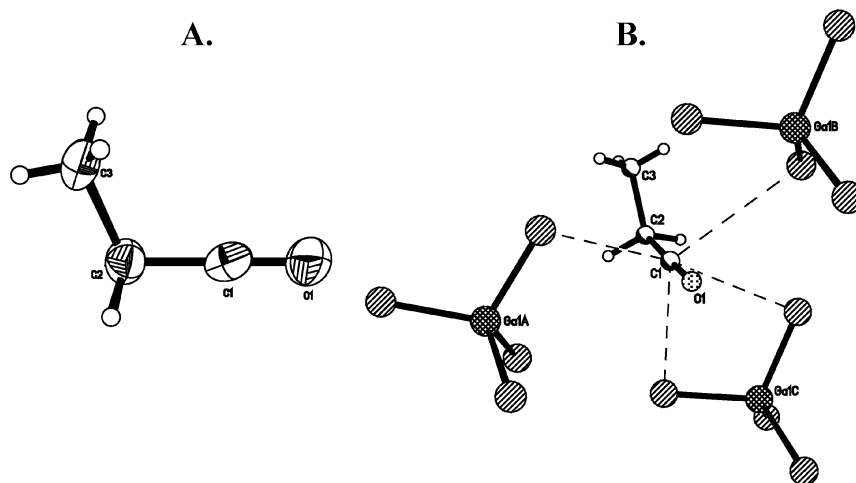
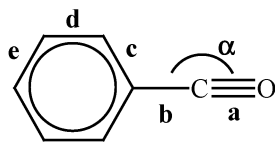


Fig. 1 (A) ORTEP diagram (50% probability ellipsoids) of Et–CO⁺ showing the linear coordination of carbon monoxide. (B) Unit cell fragment showing the distorted tetragonal coordination of three GaCl₄[−] about the cationic center.

Table 2 Geometric and IR parameters^a of the aromatic aroyl cations

Cation-anion pair (method)	<i>a</i> /Å	<i>b</i> /Å	<i>α</i> /deg	<i>c</i> /Å	<i>d</i> /Å	<i>e</i> /Å	<i>ν</i> (CO)/cm ⁻¹
<i>p</i> -MeC ₆ H ₄ -C≡O ⁺ SbCl ₆ ⁻ (A)	1.116(2)	1.391(2)	179.2(2)	1.405(2)	1.378(2)	1.400(2)	2220^b
	1.10(1)Ref. 4	1.40(1)Ref. 4	179(1)Ref. 4	1.40(1)Ref. 4	1.36(1)Ref. 4	1.39(1)Ref. 8	—
Mes-C≡O ⁺ SbCl ₆ ⁻ (A)	1.121(4)	1.375(4)	178.1(4)	1.420(3)	1.368(4)	1.397(4)	2203^b
Me ₃ C ₆ -C≡O ⁺ SbF ₆ ⁻ (B)	1.11(1)	1.39(1)	178(1)	1.42(1)	1.39(1)	1.42(2)	2197
<i>p</i> -MeOC ₆ H ₄ -C≡O ⁺ SbF ₆ ⁻ (B)	1.125(8)	1.375(9)	177.6(7)	1.410(9)	1.360(9)	1.396(9)	2215
<i>p</i> -FC ₆ H ₄ -C≡O ⁺ SbF ₆ ⁻ (B)	1.113(5)	1.391(5)	178.9(5)	1.395(6)	1.366(6)	1.374(6)	2226

^a Reliable data used for discussion are given in bold; the actual precision of geometric parameters for Mes-C≡O⁺SbCl₆⁻, *p*-MeOC₆H₄-C≡O⁺SbF₆⁻ and *p*-FC₆H₄-C≡O⁺SbF₆⁻ is higher because these are averaged over two symmetrically independent molecules. ^b For the corresponding SbF₆ salt.

The structures of the *p*-methyl and 2,4,6-trimethylbenzoyl cations as well as the fluoro-substituted derivative were established to good experimental precision, whereas the permethylated and methoxy structures were affected by crystallographic disorder. The problem is especially pernicious in the case of the permethylated cation in which a small fraction (less than 10%) of the disk-shaped cations has the methyl and carbonyl groups permuted. This disorder compromised the reliability of the structural parameters owing to the (effective) shift of the carbonyl carbon toward the oxygen and away from the benzene ring. Nevertheless, the crystallographic data in Table 2 provide sufficient structural information to discuss the principal structural and electronic features of aromatic aroyl carbocations.

The ORTEP diagram in Fig. 2(A) of the fluorobenzoyl moiety in *p*-FC₆H₄-CO⁺ SbF₆⁻ is a typical representation of the basic 3 atom fragment C_α-C-O showing the linear coordination of CO to the aromatic (substituent) group; and Fig. 2(B) emphasizes the tetragonal disposition of SbF₆⁻ anions (*r*_{C...F} 2.69–2.94 Å) about the cationic carbon center.¹⁰

Discussion

I. Sigma binding of carbon monoxide in aliphatic acyl cations

The nature of the alkyl coordination in the series of acyl cations (Table 1) is revealed in the variation of two structural parameters: (i) the carbonyl bond length (*r*_{CO}) and (ii) the bonding distance to the alkyl group (*r*_{C_α}). As expected for a

linear 3-center array, the variation of *r*_{CO} runs counter to that in *r*_{C_α}, that is, the general trends in *r*_{CO} and *r*_{C_α} are opposed.¹¹ Furthermore, the correlation of the carbonyl bond length *r*_{CO} with the carbonyl stretching frequency *ν*_{CO} has a qualitative trend¹² which is opposite to expectations of the well-recognized bond-strength/bond-order interrelationship.¹¹ Therefore, let us now normalize the structural parameters (*r*_{*i*}) to the bond orders (*n*_{*i*}) as described by Pauling.¹³

In Table 3,¹³ the calculated carbonyl bond order encompasses a rather narrow range centered around *n*_{CO} = 2.72, whereas the alpha bond to the alkyl substituent is significantly more variant around *n*_{C_α} = 1.22. It is thus interesting to note that the total bond order (Σ*n*) is rather close to 4 (required by the simple octet rule) with one exception, that is, Σ*n* for the isopropyl derivative is clearly less than 4.^{14–19} In other words, the Pauling approach alone does not adequately account for the electronic effects of the isopropyl group relative to those of either methyl or ethyl.

The inspection of Table 3 reveals that the bond order *n*_{C_α} for isopropyl is unusually low and largely responsible for (a) the total bond order Σ*n* less than 4, and (b) the strong non-linear deviation of *r*_{C_α}. Since the Pauling paradigm of bond order in Table 3 is mainly focussed on the variation of the π component,^{14c} the shortening of *r*_{CO} in the isopropyl derivative is not adequately compensated in the (excess) lengthening of *r*_{C_α}. The discrepancy is seen in Table 3 for isopropyl with Σ*n* substantially less than 4, and this indicates that the π component alone is not sufficient to satisfy the octet requirement.^{14d} Since earlier

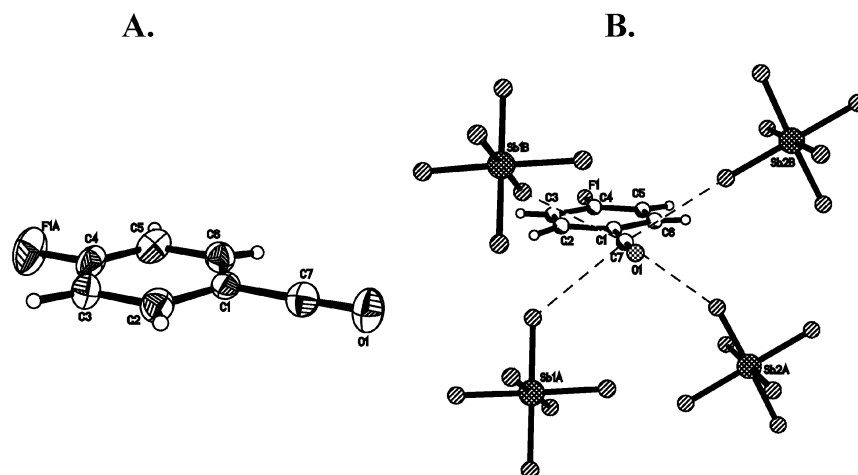


Fig. 2 (A) ORTEP diagram (50% probability ellipsoids) of the *p*-fluorobenzoyl cation showing the linear coordination of carbon monoxide. (B) Tetragonal coordination of SbF₆⁻ anions about the cationic center.

Table 3 Pauling bond orders for aliphatic acyl cations

Alkyl-CO ⁺	n_{CO}	$n_{\text{C}\alpha}$	\sum_n
Me-CO ⁺	2.69(3)	1.32(2)	4.01(4)
Et-CO ⁺	2.74(4)	1.29(4)	4.03(6)
<i>i</i> -Pr-CO ⁺	2.75(3)	1.11(2)	3.86(4)

physical-organic studies²⁰ indicated that the σ -donor property of the isopropyl group is enhanced relative to that of either methyl or ethyl, we suggest that the electron deficit (of ~ 0.3 e) is compensated by an inductive effect operating through the σ bond.^{14d} Such a σ -inductive effect also accounts for the inverse order in the carbonyl stretching frequencies,^{13,21} and is in complete accord with the previous conclusions about the bonding in “nonclassical” metal carbonyls.²

II. Pi binding of carbon monoxide in aromatic aroyl cations

In the substituent effect on the series of aroyl structures presented in Table 2, the general trend of the carbonyl bond length (r_{CO}) is opposed to the trend for aryl separation from CO ($r_{\text{C}\alpha}$) which is consistent with the expectations of such compensating changes in bond lengths for the linear $\text{C}\alpha\text{-C-O}$ unit. However, both are opposite to the trends in r_{CO} and $r_{\text{C}\alpha}$ for the aliphatic acyl cations as presented in Table 1. Most revealingly, the trend in the bond correlation for the aroyl cations is also opposed to that for acyl cations.¹² Indeed, the inverse slope is the one expected for the Pauling analysis based on predominant π conjugation, and it is in accord with the π backbonding generally observed in transition metal carbonyls.

In aromatic aroyl cations, the electronically unsaturated (cationic) center adopts the linear sp -hybridized configuration as shown by all α values in Table 2 very close to 180° . Most importantly, the carbonyl bonds (r_{CO}) are 1–2 pm longer than those in the aliphatic acyl cations owing to π conjugation with the aromatic substituent; and this elongation is consistent with the reduced IR stretching frequency of the carbonyl group by $\Delta \nu_{\text{CO}} = 30\text{--}100\text{ cm}^{-1}$. Specifically in the *p*-methylbenzoyl cation, π conjugation achieves almost 100% efficiency as follows from the α bond length of $r_{\text{C}\alpha} = 1.391\text{ \AA}$, which coincides with the standard value of 1.39 \AA for the aromatic conjugated carbon–carbon π bond.¹⁶ Such a conjugation is accompanied by an elongation of the carbonyl bond by $\Delta r_{\text{CO}} = 0.7\text{--}1.3\text{ pm}$ relative to that observed in the aliphatic acyl cations, as well as a significant quinonoidal distortion of the benzenoid ring.²² As expected, the presence of two additional methyl groups as in the mesitoyl cation further increases π conjugation by the bond length changes of $\Delta r_{\text{CO}} = 0.6\text{ pm}$ and $\Delta r_{\text{C}\alpha} = 1.6\text{ pm}$, together with further quinonoidal distortion.²³ The introduction of the strong π -donor substituent as in the anisoyl cation promotes the development of π conjugation since the Ar–CO bond of $r_{\text{C}\alpha} = 1.125\text{ \AA}$ is the longest and the quinonoidal distortion is the greatest. Remarkably, this structural change in $\text{MeOC}_6\text{H}_4\text{CO}^+$ is not reflected in the decreased $\nu_{\text{CO}} = 2215\text{ cm}^{-1}$, and results in its poor correlation.²⁴ At the other extreme, the introduction of fluorine as an electron-acceptor substituent in *p*- $\text{FC}_6\text{H}_4\text{CO}^+$ results in the least π -conjugated carbocationic center with the shortest $r_{\text{C}\alpha} = 1.112\text{ \AA}$ (and with an increased stretching frequency of $\nu_{\text{CO}} = 2226\text{ cm}^{-1}$).²⁵ The computation of the Pauling bond order in

Table 4²⁶ shows that π conjugation is sufficient to complete the octet requirement with \sum_n clearly equal to 4.0 for all the aromatic aroyl cations in contrast to the values of \sum_n for the acyl cations listed in Table 3.

Summary and conclusions

Highly electrophilic oxocarbenium structures R-CO^+ were synthesized from the corresponding acid halides (using strong Lewis acids or silver(I) salts) and isolated as crystalline solids in the presence of low-nucleophilic counteranions such as SbCl_6^- , SbF_6^- or GaCl_4^- . Precise low-temperature X-ray structural data were obtained for the aliphatic carbocations: $\text{CH}_3\text{-C}\equiv\text{O}^+\text{SbF}_6^-$ and $\text{MeCH}_2\text{-C}\equiv\text{O}^+\text{GaCl}_4^-$, which together with the latest literature data⁷ on $\text{Me}_2\text{CH-C}\equiv\text{O}^+\text{SbCl}_6^-$ comprise the first reliable series of structural measurements on these important electronically unsaturated species as the key intermediates of Friedel–Crafts reaction. For the aromatic analogs, the structure of *p*- $\text{Me-C}_6\text{H}_4\text{-C}\equiv\text{O}^+\text{SbCl}_6^-$ was re-determined with superior precision and its 2,4,6-trimethyl and 2,3,4,5,6-pentamethyl analogs were studied for the first time. The aromatic series was also extended to an even more electron-donor substituted benzoyl cation such as *p*- $\text{MeO-C}_6\text{H}_4\text{-C}\equiv\text{O}^+$ as well as electron-poor substituted *p*- $\text{F-C}_6\text{H}_4\text{-C}\equiv\text{O}^+$. Solid-state IR spectra were measured for the all carbocations investigated.

For both series of the oxocarbenium structures, the following general structural features are confirmed: (a) significant triple character of the carbonyl bond as follows from its length ($1.10\text{--}1.11\text{ \AA}$ for the aliphatic and $1.11\text{--}1.12\text{ \AA}$ for the aromatic oxocarbenium structures) and from the enhanced IR stretching frequency ($\sim 2300\text{ cm}^{-1}$ for the aliphatic and $\sim 2200\text{ cm}^{-1}$ for the aromatic series); (b) significant shortening of the adjacent single bond with $r_{\text{C}\alpha}$ (up to 1.42 and 1.37 \AA , in the aliphatic and the aromatic cations, respectively) due to electronic $\sigma\text{-}\pi$ hyperconjugation of the aliphatic moiety and $\pi\text{-}\pi$ conjugation of the aromatic moiety with the electronically deficient carbocationic center; (c) the sp^1 -hybridized linear configuration of the carbocationic centers characterized by the α angle in $\text{C}\alpha\text{-C}\equiv\text{O}$ close to 180° .

In addition, for the aliphatic acyl cations, it was found that the $\sigma\text{-}\pi$ hyperconjugation is not as strong as it was earlier deduced from less precise data. Nevertheless, hyperconjugation in $\text{CH}_3\text{-C}\equiv\text{O}^+$ and $\text{MeCH}_2\text{-C}\equiv\text{O}^+$ cations can be qualitatively estimated as 60% of the complete (1-electron benzenoid) conjugation that results in the shortest value of 1.42 \AA for this bond type. The effectiveness of the $\sigma\text{-}\pi$ hyperconjugation is significantly reduced in $\text{Me}_2\text{CH-C}\equiv\text{O}^+$, owing to the availability of only a single $\text{C}\alpha\text{-H}$ bond. The geometry of the carbonyl group in acyl cations is almost unaffected by hyperconjugation, but shows significant bathochromic shifts in the IR spectra with the number of electron-donor groups at the β carbon center, that is, IR frequency of the carbonyl group decreases in the order: $\text{H}_3\text{C-C}\equiv\text{O}^+ > \text{MeCH}_2\text{-C}\equiv\text{O}^+ > \text{Me}_2\text{CH-C}\equiv\text{O}^+$, which is opposite to the degree of the hyperconjugation. This somewhat paradoxical spectroscopic behavior can be explained from the linear sp configuration of the carbocationic center in which the σ -bonding orbital of the single bond interacts with the σ -antibonding orbital of the carbonyl group.

Aromatic aroyl cations show $\pi\text{-}\pi$ conjugation between the carbocationic center and the adjacent benzene ring, which increases progressively with the aryl donicity. The shortening of the single (conjugated) bond C-C of up to 1.37 \AA with corresponding elongation of the triple bond $\text{C}\equiv\text{O}$ of up to 1.125 \AA tracks the decreasing IR (ν_{CO}) frequency. Conjugation also has a pronounced quinonoidal effect on the geometry of the benzene ring (which is less than that deduced earlier from less precise data). Interestingly, the electronegative methoxy oxygen has a significant enhancing effect on the IR frequency

Table 4 Pauling bond orders for aromatic aroyl cations

Ar-CO ⁺	$n_{\text{C}\alpha}$	n_{CO}	\sum_n
$\text{MeC}_6\text{H}_4\text{-CO}^+$	2.62(2)	1.34(1)	3.97(2)
2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{-CO}^+$	2.58(3)	1.41(3)	3.99(4)
<i>p</i> - $\text{MeOC}_6\text{H}_4\text{-CO}^+$	2.55(6)	1.41(6)	3.96(9)
<i>p</i> - $\text{FC}_6\text{H}_4\text{-CO}^+$	2.65(4)	1.31(3)	3.96(5)

of the carbonyl group, apparently through the aforementioned σ - σ^* inductive mechanism. By contrast, the electron-accepting fluoro substituent reduces the conjugation of the carbonyl group and raises the IR frequency to the most extreme values in the series.

Experimental

Materials

The acyl halides (acetyl chloride, acetyl fluoride, propionyl chloride, *p*-toluyl chloride, *p*-anisoyl chloride and *p*-fluorobenzoyl chloride) were from Aldrich. 2,4,6-Mesityl chloride and pentamethylbenzoyl chloride were prepared from the corresponding carboxylic acids (Aldrich) by treatment with oxalyl chloride (Aldrich). SbCl_5 , SbF_5 and AgSbF_6 from Aldrich were used without additional purification. Dichloromethane, benzene and hexane were purified according to published procedures.²⁹ 1,1,2-Trifluoroethane (Freon 113) from Aldrich was used without additional purification.

Synthesis of 2,4,6-trimethylbenzoyl chloride and pentamethylbenzoyl chloride

The corresponding 2,4,6-trimethylbenzoic (2 g or 12 mmol) or pentamethylbenzoic acid (10 mmol) were dissolved in 10 ml of benzene and a large excess (5 times) of oxalyl chloride was introduced (7.7 and 6.6 g, respectively) under stirring. The mixture was stirred under an argon atmosphere for 3 h. The solvent and the residual oxalyl chloride were removed under vacuum, and the remainder of the solution was distilled under

reduced pressure (b.p. 121 and 140 °C at 20 mm Hg, respectively; yield 50–55%).

Syntheses of alkyl and aryloxocarbonium salts

The oxocarbonium salts were prepared using literature methods involving two general synthetic procedures described as methods (A) and (B) in eqns. (1) and (2). Method (A) was used for acyl and aroyl halides with either $\text{X} = \text{F}$ and PF_5 , BF_3 , SbF_5 , AsF_5 or $\text{X} = \text{Cl}$ and AlCl_3 , GaCl_3 , SbF_5 . Method B was used for acyl and aroyl chlorides and silver(I) PF_6^- , BF_4^- , SbF_6^- , AsF_6^- . It is important to mention that the target oxocarbonium salts are *extremely* sensitive to air. Their successful isolation required highly pure reagents and extreme precautions against moisture. The acid halides were always freshly distilled and anhydrous silver salts were carefully dried *in vacuo* (including cautious heating) prior to synthesis. The solvents were additionally passed through a column containing activated molecular sieves immediately prior to use. Generally, it is highly recommended to carry out all sample manipulations under an argon atmosphere in a rigorously water and air-free drybox.

Methyloxocarbonium hexachloroantimonate (method A).

Freshly distilled acetyl chloride (0.785 g, 10 mmol) was dissolved in 10 ml of dry dichloromethane under an argon atmosphere, and the solution was cooled to 0 °C. Under careful stirring, a solution of 5.98 g of SbCl_5 (20 mmol) in 10 ml of dry dichloromethane was introduced. After 15 min of the continuous stirring, a white crystalline precipitate was collected, washed with cold CH_2Cl_2 and dried under vacuum. Single

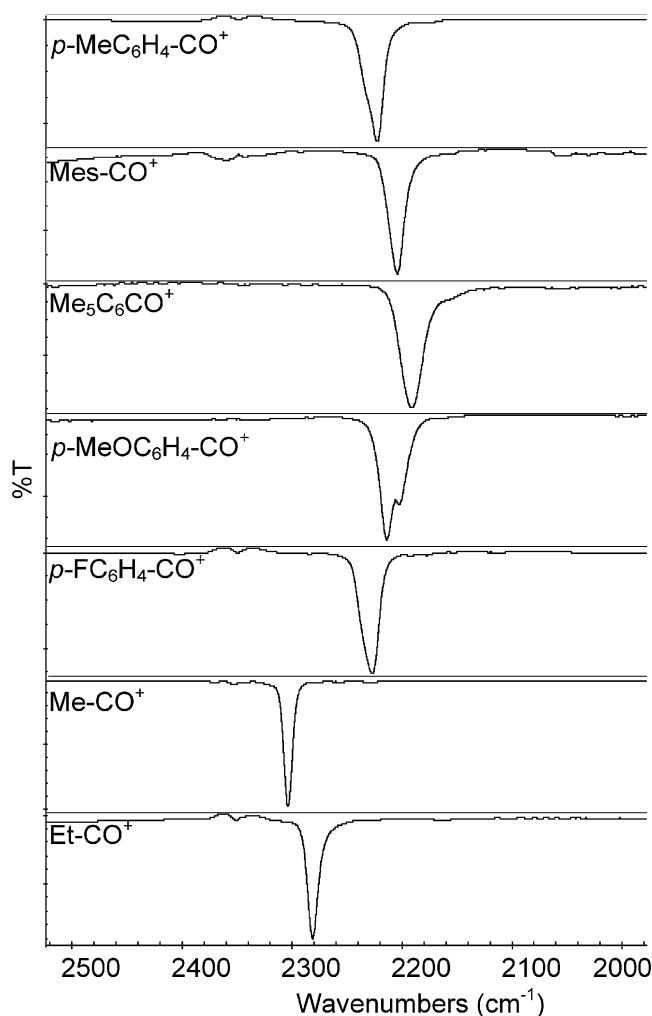


Fig. 3 Reflectance IR spectra (partial) of aroyl and acyl salts in the region of CO stretching vibrations.

Table 5 Crystallographic parameters and the details of the structure refinements

Compound	MeCO ⁺ SbF ₆ [−]	EtCO ⁺ GaCl ₄ [−]	<i>p</i> -TolCO ⁺ SbCl ₆ [−]	MesCO ⁺ SbCl ₆ [−]	Me ₅ C ₆ CO ⁺ SbF ₆ [−] · CH ₂ Cl ₂	<i>p</i> -MeOC ₆ H ₄ CO ⁺ SbF ₆ [−]	<i>p</i> -FC ₆ H ₄ CO ⁺ SbF ₆ [−]
Formula	C ₂ H ₃ F ₆ OSb	C ₃ H ₅ Cl ₄ GaO	C ₈ H ₇ Cl ₆ OSb	C ₁₀ H ₁₁ Cl ₆ OSb	C ₁₃ H ₁₇ Cl ₂ F ₆ OSb	C ₈ H ₇ F ₆ O ₂ Sb	C ₇ H ₄ F ₇ OSb
<i>M</i>	278.79	268.59	453.59	481.64	495.92	370.89	358.85
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	5.7299(7)	7.146(1)	11.7482(7)	9.2849(5)	7.6218(6)	19.061(1)	12.586(1)
<i>b</i> /Å	7.7373(9)	9.487(2)	10.2038(6)	25.038(1)	12.7753(9)	10.4108(8)	12.396(1)
<i>c</i> /Å	7.7479(9)	13.931(2)	12.4473(8)	14.9209(7)	18.242(1)	28.690(2)	13.079(1)
<i>β</i> /°	100.187(2)	97.909(4)	93.428(1)	104.665(1)	90.641(1)	91.537(2)	92.252(2)
<i>U</i> /Å ³	338.08(7)	935.4(3)	1489.5(2)	3355.8(3)	1776.2(2)	5691.2(8)	2038.9(4)
<i>Z</i>	2	4	4	8	4	20	8
<i>D</i> _c /g cm ^{−3}	2.739	1.907	2.023	1.907	1.855	2.164	2.338
<i>N</i> _{ref} (collected)	3629	8621	15992	36634	19127	31114	22251
<i>R</i> _{int}	0.0254	0.0485	0.0218	0.0219	0.0212	0.0342	0.0461
<i>N</i> _{ref} (indep.)	1150	3008	4714	10746	5693	9116	6591
<i>N</i> _{ref}	1108	1829	4366	9254	5180	7508	4157
[<i>I</i> > 2σ(<i>I</i>)]							
<i>R</i> ₁	0.0201	0.0454	0.0202	0.0276	0.0295	0.0661	0.0437
<i>wR</i> ₂	0.0502	0.0942	0.0496	0.0630	0.0723	0.1626	0.0914

crystals suitable for X-ray analysis were obtained by slow cooling of the dry dichloromethane solution initially saturated at 40 °C.

Acetyl hexafluoroantimonate (method A). Freshly distilled acetyl fluoride (0.62 g, 10 mmol) was dissolved in 10 ml of Freon 113 under an argon atmosphere, and the solution was cooled to −20 °C. An equimolar amount of SbF₅ (2.17 g) was introduced with careful stirring. After 15 min of continuous stirring, a white crystalline precipitate was collected, washed with cold Freon and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the Freon solution under an argon atmosphere.

Propionyl tetrachlorogallate (method A). Freshly distilled propionyl chloride (0.185 g, 2 mmol) was dissolved in 10 ml of dry dichloromethane under an argon atmosphere. 0.352 g of GaCl₃ (2 mmol) was added into the stirred solution which was then cooled to −40 °C. A white crystalline precipitate was collected, washed out with cold CH₂Cl₂ and dried under vacuum. Single crystals suitable for X-ray analysis were obtained by slow evaporation (2 h) of the dichloromethane solution.

4-Toluoyl hexachloroantimonate (method A). Freshly distilled *p*-toluoyl chloride (0.46 g, 3 mmol) was dissolved in 15 ml of dry dichloromethane under an argon atmosphere. Under careful stirring, 5 ml of dichloromethane solution containing 0.89 g (3 mmol) of SbCl₅ were introduced. The solution was covered with a layer of dry *n*-hexane (15 ml) and allowed to stand at −40 °C. Well-formed crystals of the target oxocarbenium salt were collected at the solvent interface after 3 days.

2,4,6-Mesityl hexachloroantimonate (method A). Freshly prepared 2,4,6-trimethylbenzoyl chloride (90 mg, 0.5 mmol) were dissolved in 7 ml of dry dichloromethane under an argon atmosphere. Under careful stirring, 5 ml of dichloromethane solution containing 0.14 g (0.5 mmol) of SbCl₅ were introduced. The solution was covered with a layer of dry *n*-hexane (15 ml) and allowed to stand at −40 °C. Well-formed crystals of the target oxocarbenium salt were collected at the solvent interface after 2 days.

Syntheses of pentamethylbenzoyl, 4-methoxybenzoyl, and 4-fluorobenzoyl hexafluoroantimonates (method B). Anhydrous silver(I) salt AgSbF₆ (0.24 g, 0.7 mmol) were dissolved in 15 ml

of dry dichloromethane. An equimolar amount of the corresponding aryl halide (0.147, 0.120 and 0.111 g, respectively) was then added under stirring as a solution in a limited amount (~5 ml) of dry dichloromethane. Stirring was continued for 10 min, then the AgCl precipitate was filtered off. Crystals suitable for X-ray study were obtained by slow evaporation of the filtrate (6–12 h) under an argon atmosphere.

Carbonyl stretching frequencies

Crystalline samples of the oxocarbenium salts were mounted directly on the germanium sampling plate of the single-reflection HATR (Smart Miracle, Pike Technology) under an argon atmosphere, and the infrared spectra (Fig. 3) were measured with a Nexus 470 FT-IR (Thermo Nicolet). Alternatively, crystals for X-ray crystallographic analysis suspended in mineral oil were used, and the mineral oil background digitally subtracted.

X-Ray crystallography†

The intensity data for all the compounds were collected with a Siemens/Bruker SMART diffractometer equipped with an APEX CCD detector using MoKα radiation (λ = 0.710 73 Å), at −150 °C. In all cases, a semi-empirical absorption correction was applied.²⁷ The structures were solved by direct methods and refined by full matrix least-squares procedure²⁸ with IBM Pentium and SGI O₂ computers. X-Ray structure details of the various salts are compiled in Table 5.

Acknowledgements

We thank the Robert A. Welch Foundation and the National Science Foundation for financial support.

References

- (a) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, NY, 5th edn., 1988; (b) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1979, **101**, 783; (c) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939; (d) See also: J. P. Collman and L. S. Hegeudus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980, p. 27.

† CCDC reference numbers 239194–239200 and 249788. See <http://www.rsc.org/suppdata/nj/b4/b407654k/> for crystallographic data in.cif or other electronic format.

- 2 P. K. Hurlburt, J. J. Rack, J. S. Luck, S. F. Dec, J. D. Webb, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc.*, 1994, **116**, 10003.
- 3 G. A. Olah, S. J. Kuhn, W. S. Tolgyesi and E. B. Baker, *J. Am. Chem. Soc.*, 1962, **84**, 2733.
- 4 (a) B. Chevrier, J.-M. Le Carpentier and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 2673; (b) B. Chevrier, J.-M. Le Carpentier and R. Weiss, *J. Am. Chem. Soc.*, 1972, **94**, 5718.
- 5 F. P. Boer, *J. Am. Chem. Soc.*, 1968, **90**, 6706.
- 6 The isolation and X-ray crystallography of the resultant oxocarbenium hydrates (identified as α,α -dihydroxycarbonium ions) will be reported separately.
- 7 Our attempts to obtain improved data on the molecular geometry of the $\text{Me-C}\equiv\text{O}^+\text{SbCl}_6^-$ salt (earlier studied by Le Carpentier and Weiss^{8a}) was not quite successful because of the intrinsic racemic twinning of these crystals.
- 8 (a) J.-M. Le Carpentier and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 1421; (b) J.-M. Le Carpentier and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 1430.
- 9 G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien and E. B. Baker, *J. Am. Chem. Soc.*, 1963, **85**, 1328.
- 10 (a) For an earlier discussion, see: T. Laube, *Chem. Rev.*, 1998, **98**, 1277; (b) See also: S. V. Lindeman and J. K. Kochi, *Cryst. Growth Design*, 2004, **4**, 563. Note that the arenediazonium cations are isoelectronic to aroylium cations and their salts are likely to be isostructural.
- 11 (a) For a lucid presentation of this electroneutrality principle, see: F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, NY, 5th edn., 1988, p. 57; (b) See table of bond dissociation enthalpies listed in P. W. Atkins, *Physical Chemistry*, Freeman, San Francisco, CA, 1978, p. 111.
- 12 Similarities in experimental conditions of these closely related cation salts minimize the systematic errors in the X-ray crystallography and thus the small differences in the bond lengths (Tables 1 and 2) are significant enough to reveal structural changes since we are not optimistic that more precise data on those highly reactive crystals will be forthcoming. As such, the qualitative trend is revealed by the extremes, which, in the case of acyl cations, is $\text{CH}_3\text{-CO}^+$ compared to $i\text{-Pr-CO}^+$ and in the case of aroyl extremes are $p\text{-FC}_6\text{H}_4\text{-CO}^+$ compared to $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{-CO}^+$ (with $p\text{-MeOC}_6\text{H}_4\text{-CO}^+$ excepted). Note, however, the more compelling comparisons of bond orders for acyl and aroyl cations are given by \sum_n in Tables 3 and 4 (*vide infra*).
- 13 (a) L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960, p. 239; (b) According to Pauling, the bond order n is related to the bond distance r_i by the relationship: $n_i = 10 \cdot \exp[(r_1 - r_i)/K]$ where r_1 is the single bond distance, r_i is the observed distance, and K is an empirical constant. For the carbonyl bond, $r_1 = 1.43 \text{ \AA}$ and $K = 0.75$. For the bond to alkyl, $r_1 = 1.48 \text{ \AA}$ and $K = 0.50$, which includes the correction for the change in covalent radius with hybridization. See, for example: S. M. Hubig, S. V. Lindeman and J. K. Kochi, *Coord. Chem. Revs.*, 2000, **200**, 831. The calculated bond orders are presented in the Table 3 with esds in parentheses.
- 14 From a slightly different perspective, consider the linear cationic unit¹⁵ $(\text{C-C-O})^+$ as a 3-center-6-electron assembly in which: (i) the carbonyl bond $r_{\text{CO}} = 1.11 \text{ \AA}$ (ave.) is significantly shorter than the standard bond length of the carbonyl double bond (C=O , 1.21 \AA);¹⁶ (ii) the alkyl-CO bond with $r_{\text{C}\alpha} = 1.42 \text{ \AA}$, for Me-CO^+ and Et-CO^+ in Table 1 is also among the shortest single bonds relative to 1.48 \AA as the benchmark for $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^1)$ hybridized centers in (for example) methylacetylene;¹⁶ (iii) the computed (Pauling) bond orders for Me-CO^+ and Et-CO^+ , Table 3,^{13b} show that oxygen contributes an additional 1.4 e to promote the shortened r_{CO} (via the 2p lone pairs),^{17a} and the $\text{Me}(\text{Et})$ group likewise contributes an additional 0.6 e to the shortened $r_{\text{C}\alpha}$ bond (via hyperconjugation).^{17b} Basically, both of these added contributions invoke a π release mechanism to fulfill the "octet" requirement (*i.e.* $\sum_n = 4.0$) for the shortened r_{CO} and $r_{\text{C}\alpha}$ bonds. On the other hand, \sum_n is only 3.86 for $i\text{-Pr-CO}^+$, and the deficit of 0.3 e can be attributed to the diminished hyperconjugation of the i -propyl group,¹⁹ this deficiency being made up by its increased σ bonding characteristics²¹.
- 15 Fig. 1 and Fig. 2 locate the center of positive charge on the central (carbonyl) carbon atom.
- 16 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
- 17 (a) The terminal oxygen 2p_y and 2p_z orbitals. Note also that the carbonyl bonds in Me-CO^+ and Et-CO^+ compare with $r_{\text{CO}} = 1.07 \text{ \AA}$ in an authentic ($\text{C}\equiv\text{O}$) triple bond¹⁸; (b) Hyperconjugation is related to the number of α -hydrogens owing to the cylindrical symmetry of the linear carbonyl group. The observed lengths of the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^1)$ bonds (1.42 \AA) are much shorter than the lengths of other hyperconjugated bonds, $[\text{C}(\text{sp}^3)\text{-C}(\text{sp}^2) = 1.44 \text{ \AA}]$ observed in aliphatic carbocations.¹⁹ In fact, these are the shortest values for single C-C bonds including an sp^3 -hybridized carbon atom (*i.e.* in absence of π conjugation). This remarkable shortening indicates an unusually high degree of hyperconjugation in the Me-CO^+ and Et-CO^+ , which can be estimated at 60% (taking the degree of electronic conjugation in benzene ring for a 100% standard) according to Pauling's formula.¹³ The $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^1)$ bonds in Me-CO^+ and Et-CO^+ are also remarkably shorter than the corresponding bond in $i\text{-Pr-CO}^+$ measured in the accurate study by Strauss *et al.*² ($1.458 \pm 0.004 \text{ \AA}$). This can be explained by the different number of C-H bonds available for the hyperconjugation in these cations. The most favorable configuration requires two σ orbitals of C-H bonds independently overlapping with two mutually orthogonal π orbitals of the triple bond. Therefore, the molecular structure of Et-CO^+ cation is optimal for the hyperconjugation, and the presence of an extra C-H bond in Me-CO^+ analog cannot contribute more to the effect. At the opposite extreme, the availability of only one C-H σ orbital in $i\text{-Pr-CO}^+$ cation greatly diminishes the efficiency of the hyperconjugation.
- 18 Considering the covalent radii of carbon and oxygen to be constant, extrapolation from standard values¹⁶ 1.54 and 1.43 \AA for single bonds C-C and C-O, respectively, 1.32 and 1.21 \AA for double bonds C=C and C=O (*i.e.* -0.22 \AA each), respectively, and 1.18 \AA for triple bond $\text{C}\equiv\text{C}$, gives 1.07 \AA for $\text{C}\equiv\text{O}$ (*i.e.* -0.14 and -0.36 \AA each, relative to the corresponding double and single bonds, respectively).
- 19 (a) S. Hollenstein and T. Laube, *J. Am. Chem. Soc.*, 1993, **115**, 7240; (b) T. Laube, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 560; (c) T. Laube, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 349.
- 20 For example, see the inductive parameters for the Hammett and Taft linear free-energy correlations in: T. H. Lowry, and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper-Row, New York, 2nd edn., 1981, p. 137.
- 21 The decreasing strength of the carbonyl bond in acyl cations derives from the increased interaction in the order: $i\text{-Pr} > \text{Et} > \text{Me}$ of the σ orbital of the alkyl substituent with the antibonding σ^* orbital of carbonyl group as previously described by Strauss *et al.*².
- 22 (a) Such a quinonoidal distortion is shown by the shortening of the endocyclic d (1.378 \AA) as compared with c bonds (1.405 \AA) and e bonds (1.408 \AA) in Table 2; (b) For discussion of this type of quinonoidal distortion in cations, see: S. V. Lindeman, S. V. Rosokha, D. Sun and J. K. Kochi, *J. Am. Chem. Soc.*, 2002, **124**, 843; (c) Compare Le Carpentier *et al.* in refs. 4 and 8.
- 23 (a) Quinonoidal distortion with the d bond of 1.368 \AA ; (b) Extension to the pentamethyl analog suffered from disorder. Nonetheless increased π conjugation is expected based on the decrease in ν_{CO} from 2220 and 2283 cm^{-1} to 2197 cm^{-1} , from monomethyl and trimethyl to pentamethyl analogs; (c) Quinonoidal distortion with the shortest d bond = 1.360 \AA .
- 24 We tentatively suggest that this "anomaly" may arise from the inductive effect of the methoxy group which acts as a σ acceptor to diminish the population of the σ^* orbital of the carbonyl group much like that discussed with $i\text{-Pr-CO}^+$ (*vide supra*).
- 25 However, the fluorine substituent also has a noticeable mesomeric effect on the benzenoid substituent that exhibits a rather pronounced quinonoidal distortion with the d bond of 1.366 \AA .
- 26 The application of the Pauling relationship¹⁸ to aroyl cations is based on $r_1 = 1.455 \text{ \AA}$ and $K = 0.50$.
- 27 G. M. Sheldrick, *SADABS (Ver. 2.03) – Bruker/Siemens Area detector absorption and other corrections*, Bruker Analytical X-ray Systems, Madison, WI, 2000.
- 28 G. M. Sheldrick, *SHELXTL, Program Library for Structure Solution and Molecular Graphics*, v.6.12, Bruker Analytical X-ray Systems, Madison, WI, USA, 2000.
- 29 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, in *Purification of Laboratory Chemicals*, Pergamon, New York, 2nd edn., 1980.