Theoretical Study of Charge Distribution in the Benzoyl and Alkynoyl Cations

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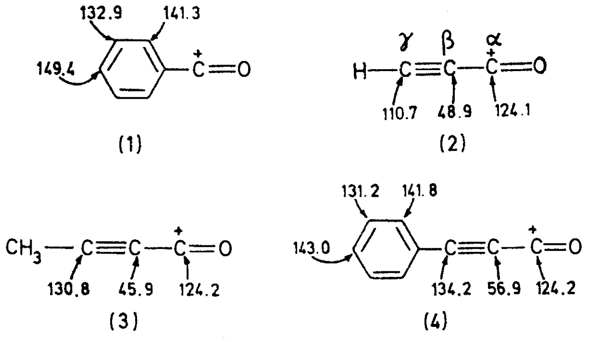
SCF-MO calculations, in the INDO approximation, have been carried out on benzoyl (1), propynoyl (2), but-2-ynoyl (3), 3-phenylpropynoyl (4), and 3-fluoropropynoyl cations (5). In each case the geometries were optimized to minimum energy. In aggreement with ^{13}C n.m.r. observations, significant charge delocalization into the phenyl rings occurs in (1) and (4). From an examination of the charge distributions, π-bond orders, and π- and σ-electron distributions it is shown that extensive delocalization of charge occurs in (2), (3), and (5), contrary to previous interpretations of ^{13}C spectra. Thus all the mesomeric forms $RC{\equiv}C{-}C{\equiv}O^+ \longleftrightarrow RC{\equiv}C{-}\overset{+}{C}{=}O \longleftrightarrow R\overset{+}{C}{=}C{=}C{=}O$ contribute significantly in (2), (3), and (5) as well as in (4), and the charge is not substantially localized on oxygen as previously claimed.

PROTON n.m.r. spectroscopy has been widely used to probe the structure and charge distribution in carbocations.[1-3] Recently ^{13}C n.m.r. spectroscopy has been used to probe more directly the charge distributions along the carbon framework.[4] Recently, Olah reported the ^{13}C n.m.r. spectra of the benzoyl cation (1) [5] and alkynoyl cations (2)—(4).[6] It was concluded from an examination of the ^{13}C chemical shifts (shown in the Scheme in p.p.m. from tetramethylsilane) that in (1) and (4) substantial charge delocalization into the phenyl rings occurred. Surprisingly, however, the authors also concluded that the charge was mainly localized on the oxygen atom in (2) and (3) and that vinylic resonance hybrids made no appreciable contribution.[6]



SCHEME

However, parallels between ^{13}C chemical shifts and charge distribution must be viewed cautiously because ^{13}C chemical shifts depend on hybridization, charge, and anisotropic diamagnetic and paramagnetic shielding effects.[7] Furthermore, the choice of model compounds, with which one compares the chemical shifts of (1)—(4) presented some difficulty. Thus, we decided to perform a series of SCF-MO calculations, in the INDO approximation,[8,9] on cations (1)—(4), as well as the 3-fluoropropynoyl cation (5), to probe the charge distribution as a test of the conclusions derived from the ^{13}C n.m.r. data. To allow a rigorous test, within the INDO framework, geometry optimization calculations were performed in a systematic manner.

RESULTS

Geometry optimization was carried out as described previously.[11-18] All calculations employed the CINDO program, QCPE number 141. The optimized geometries and charge distributions of carbocations (1)—(5) are given in the Figure. All bond lengths and bond angles were systematically varied. The minimum in the energy varied by <0.05 kcal mol^{-1}. Thus the bond lengths have been obtained to 0.001 Å. In (1) and (4) the substituent axes bisect the ring angles.

The results clearly indicate substantial charge delocalization occurs in cations (2) and (3) (in contrast to Olah's conclusions based on ^{13}C n.m.r. studies [6]) as well as in cations (1), (4), and (5). The following items support this conclusion: (i) substantial positive charge is calculated at C_γ in (2) and (3); (ii) the magnitude of the positive charge calculated at C_γ is about the same for (2)—(4); (iii) the magnitude of the charge on oxygen is about the same for (1)—(5). The charge is almost zero. Considering that the

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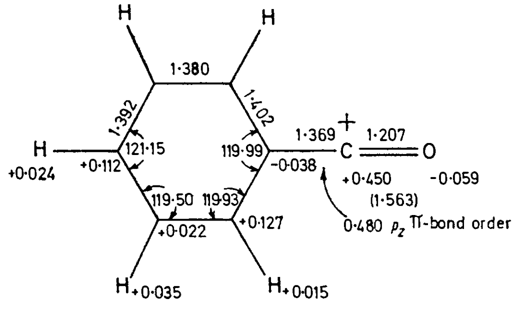

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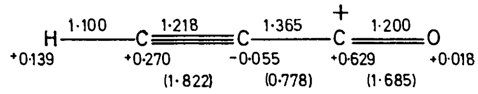

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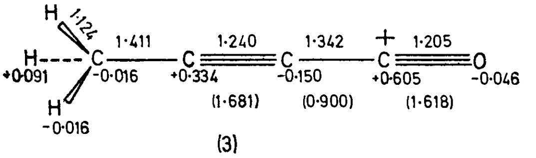

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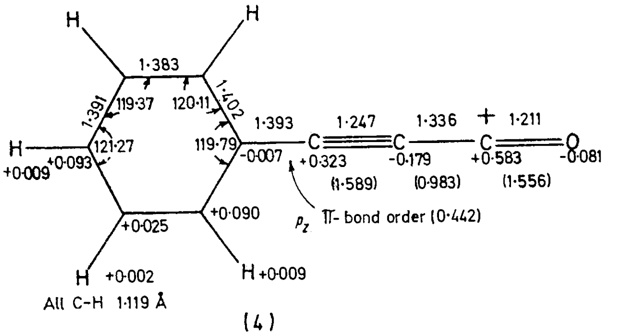

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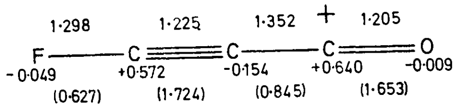


(5)

Optimized geometries, charge distributions, and π-bond orders of cations (1)—(5). Numbers in parentheses are the sum of the p_z and p_y π-bond orders

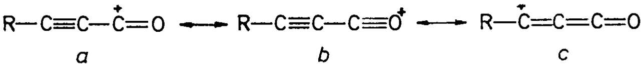
carbonyl oxygens in the neutral model molecules, propenal and propynal, exhibit charges of −0.228[9] and −0.277.[10] respectively, in INDO calculations, one can conclude that the oxygen atoms of cations (1)—(5) have donated substantial π-electron density to the α-carbon. Examining the electron densities in the p_z and p_y orbitals of oxygen and the α-carbon revealed this trend. The C_α–O σ-bond remained strongly polarized towards oxygen; and (iv) The C_α–O π-bond orders in (1)—(5) and the C_β–C_α and C_γ–C_β π-bond orders in (2)—(5) were remarkably consistent (see Figure). They show that substantial π-delocalization from oxygen to C_γ occurs in (2)—(5). It is obvious that charge is highly delocalized in (2), (3), and (5) and that this delocalization resembles that in (4) [or(1)], contrary to conclusions based on ^{13}C n.m.r. shifts.[6]

Significant charge delocalization into the phenyl rings occurs in (1) and (4) in agreement with Olah's ^{13}C n.m.r. chemical shift interpretations.[6] This is clearly evident from (a) the higher charge densities calculated at the *ortho*- and *para*-positions, (b) the obvious bond alternation effect where the optimized phenyl ring geometries of (1) and (4) have a distinct quinonoid character, and (c) the p_z π-bond order alternation in the phenyl rings (see Table). No n.m.r. data is yet available on (5). However, the trend here is the same as in the other cases except that the charge at C_γ is quite high due to polarization of the C–F σ bond toward fluorine.

Conclusions.—Geometry optimized INDO calculations demonstrated that charge delocalization is extensive in alkynoyl cations (2), (3), and (5), in addition to (4). Thus, a substantial contribution is made by each of the resonance hybrids *a*—*c* in these species. There appears to be no unique difference in charge delocalization between (4) and (2), (3), or (5) over the oxygen and α, β, or γ-carbons. 'Keten-like' mesomeric forms of (1) [*i.e.* (1a)] make a substantial contribution as do the vinylogous (4b) and cumulene (4a) mesomeric forms of (4).

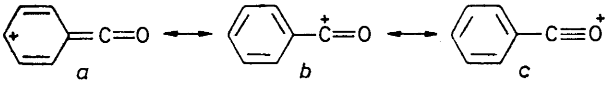
P_z π-Bond orders for phenyl rings in cations (1) and (4)

Bond	(1)	(4)
C_{ipso}–C_{ortho}	0.562	0.592
C_{ortho}–C_{meta}	0.705	0.693
C_{meta}–C_{para}	0.638	0.648


$$\underset{a}{R{-}C{\equiv}C{-}\overset{+}{C}{=}O} \longleftrightarrow \underset{b}{R{-}C{\equiv}C{-}C{\equiv}\overset{+}{O}} \longleftrightarrow \underset{c}{R{-}\overset{+}{C}{=}C{=}C{=}O}$$

(2),(3) and (5)

Calculations, of course, do not take into account solvent effects. A specific solvent may stabilize mesomeric forms (2b), (3b), or (5b) by co-ordinating to oxygen. However, if that was actually taking place, so that the charge distribution pattern was seriously changed going from the gas phase to solution, one might expect it would also occur in (4). Thus mesomeric structure (4d) should be stabilized in the same manner, and one would not expect a fundamentally different delocalization pattern for (4) *versus* (2) or (3) in



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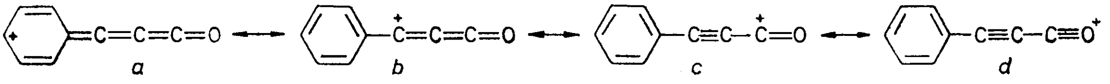

(4)

solution. Thus, INDO calculations support the expectations of simple resonance considerations for structures (1)—(5) and strongly suggest that the n.m.r. spectra[6] of (2) and (3) should be re-examined or reinterpreted.

It could be argued that other quantum chemical approaches might be more effective. Thus, preliminary MINDO/2 calculations[19] were performed on (2) and (3). As with INDO, the MINDO results predicted significant charge distribution onto C_γ and strong contributions by (2a and c) and (3a and c). Recently, *ab initio* calculations have been successfully applied to studies of the energies of isodesmic reactions involving charged and neutral species.[20–22] Radom,[23] using both the STO-3G[24] and extended 4-31G[25] basis sets, successfully predicted the $\overset{+}{\mathrm{C}}\mathrm{=O}$ bond length in the acetyl cation as 1.141 and 1.107 Å respectively *versus* experimental values of 1.108[26] and 1.109 Å[27] found in *X*-ray crystal structures. The optimized $\overset{+}{\mathrm{C}}\mathrm{=O}$ lengths in (1)—(5), as calculated by INDO, were in the range 1.200—1.211 Å. The use of the 4-31G basis set is known to be more reliable in predicting geometries of charged species,[28,29] but no optimized $\overset{+}{\mathrm{C}}\mathrm{=O}$ lengths have yet been calculated using that method for conjugated cations such as (1)—(5). Thus, comparison with INDO geometries for (1)—(5) cannot yet be made. However, conjugated systems such as (1)—(5) would be expected, on first principles, to have longer $\overset{+}{\mathrm{C}}\mathrm{=O}$ lengths than the acetyl cation.

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