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CORRELATION OF THE REACTIVITY OF COORDINATED π-HYDROCARBONS WITH ELECTRONIC PARAMETERS

III *. STABILIZATION OF THE BENZYL CATION COORDINATED TO $Cr(CO)_3$

D.W. CLACK and L.A.P. KANE-MAGUIRE

Chemistry Department, University College, Cardiff, PO Box 78, Cardiff, Wales (Great Britain)

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Summary

INDO molecular orbital calculations have been carried out on the free benzyl carbonium ion and on the coordinated cation $[(benzyl)Cr(CO)_3]^+$. The remarkable stability of the coordinated benzyl cation is shown to arise via backbonding from the chromium $d_{x^2-y^2}$ orbital into the non-bonding π-orbital of the benzyl ligand. This model is discussed in relation to previous proposals for the mode of stabilization.

Introduction

The reactivity of π-hydrocarbons is well known to be strongly modified by coordination to transition metals. Some of the most striking such observations are the rate enhancements of 10^5 and 10^3 found [1] for the solvolyses of benzyl and benzhydryl chlorides, respectively, when complexed to the $Cr(CO)_3$ moiety. Somewhat smaller rate enhancements have more recently been observed for the hydrolysis of related species such as cumyl chloride [2].

Attempts to explain the above rate enhancements have focussed on the extraordinary stability of the complexed carbonium ion in the transition state. Spectroscopic evidence [3] also confirms the greater thermodynamic stability of $[(benzyl)Cr(CO)_3]^+$ (I) compared with the free benzyl cation ($pK_R = -11.8$ and -17, respectively). This problem has attracted considerable attention, and two fundamentally different stabilization mechanisms (based largely on analogy with the related α-ferrocenyl carbonium ions [4,5]) have been proposed [6]: (i) neighbouring group participation (*d*-orbital bridging) in which there is direct interaction between a filled metal *d* orbital and a vacant *p* orbital on the car-

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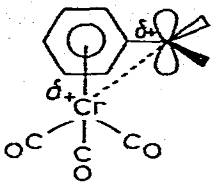
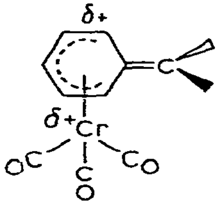
* For part II see ref. 19.

bonium ion:



(ii) metal—ring σ—π delocalization in which the α-carbonium ion is stabilized by π-conjugation with the ring:

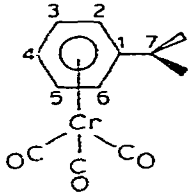


Despite efforts [2,7] to obtain experimental support for these opposing hypotheses, the nature of the stabilization remains uncertain. In the hope of clarifying the situation we have therefore carried out INDO molecular orbital calculations on the benzylcarbonium ion both free and complexed to $Cr(CO)_3$.

The results suggest that the stabilisation arises via yet another mechanism, which leads to an overall change in the structure of the benzyl moiety.

Method

The wavefunctions and associated orbital populations and atomic changes were computed for the "free" benzyl cation, and for the complex $[(benzyl)Cr(CO)_3]^+$ (I) in a number of geometrical conformations, using the established



(I)

INDO SCF molecular orbital method [8]. As before, the metal 3*d*, 4*s* and 4*p* orbitals, carbon and oxygen 2*s* and 2*p* orbitals, and hydrogen 1*s* orbitals were used as basis set in constructing the molecular orbitals.

In view of the fact that neither the benzyl cation nor the complexed cation can be isolated, initial molecular geometries were estimated from the $[(C_6H_6)Cr(CO)_3]$ species, for which X-ray structural data [9] give Cr—CO = 1.84 Å and Cr—C(ring) = 2.22 Å. The C(1)—C(7) distance was optimized at 1.41 Å and the methylene fragment was initially made to lie co-planar with the ring in the *xy* plane, with the angle C—C—H equal to 120° and C—H(methylene) = 1.09 Å. The molecular *z*-axis was made to lie along the metal—ring-centre direction. Total energy considerations showed that while this choice is valid for the free benzyl cation, complexation to $Cr(CO)_3$ leads to a bending of the CH_2 fragment (see later).

It was also necessary to consider the configuration of the CO groups with respect to the ring since $[(arene)Cr(CO)_3]$ (arene = toluene, benzene, anisole, hexamethylbenzene, *o*-toluidine) display both staggered and eclipsed configurations [9—12]. Initial calculations on I showed that both eclipsed configurations (eclipsed C(1) and eclipsed C(2) possess similar energies, but that the staggered conformation is lower in energy by some 25 kJ $mole^{-1}$. For this reason all the results are given using the staggered configuration.

Results and discussion

The total charges on the benzyl carbon atoms C(1)—C(7) are given in Table 1 for both free and complexed cations. In the free cation the formal 1 + charge on C(7) is seen to be delocalised over the entire ring, decreasing in the order C(7) $\gg$ C(4) > C(2), C(6) > C(3), C(5) $\gg$ C(1), which is consistent with normal mesomeric influences. This charge distribution is seen clearly to arise largely from differences in the π-electron density (Table 1).

Upon complexation to the $Cr(CO)_3$ moiety the large positive charge on C(7) decreases dramatically to become a slightly negative value. This result is thus fully consistent with stabilization of the benzyl carbonium ion transition state via charge delocalization. The decrease is caused by the large increase in π-electron occupancy on this atom, which more than compensates for the small loss of σ-electrons. Interestingly, the sequence of positive charges for all the ring carbon atoms is seen to be completely reversed on complexation, becoming C(1), C(3), C(5) $\gg$ C(2), C(6) > C(4) $\gg$ C(7). Again, the changes in π-electron density are responsible for this inversion, since coordination results in increased π-electron density on C(2), C(4), and C(6) while the π-occupancies of C(1), C(3), and C(5) are diminished. There is an overall loss of σ-electron density from the ring due to donation into appropriate empty orbitals on the metal.

The present calculations can be employed to test the efficacy of each of the alternative hypothesis (i) and (ii) above in explaining the stability of the coordinated benzyl cation. While both models readily rationalise the decrease in positive charge at C(7), the calculated C—C bond orders in Table 2 are clearly inconsistent with the σ—π delocalization model. This formulation might be ex-

TABLE 1

CARBON ATOMIC CHARGES AND σ- AND π-ELECTRON OCCUPANCIES FOR $[benzyl]^+$ AND $[(benzyl)Cr(CO)_3]^+$ (I)

Atom	Total charge		π-Electron density		σ-Electron density	
	$[benzyl]^+$	I	$[benzyl]^+$	I	$[benzyl]^+$	I
C(1)	0.00	+0.18	1.03	0.92	2.97	2.90
C(2)	+0.13	+0.12	0.84	0.97	3.03	2.91
C(3)	+0.09	+0.18	1.00	0.89	2.91	2.93
C(4)	+0.18	+0.11	0.77	0.99	3.05	2.91
C(5)	+0.09	+0.18	1.00	0.89	2.91	2.93
C(6)	+0.13	+0.12	0.84	0.97	3.03	2.91
C(7)	+0.28	—0.06	0.51	1.04	3.21	3.02

TABLE 2

π-BOND ORDERS FOR [benzyl]$^+$ AND [(benzyl)Cr(CO)$_3$]$^+$

Bond	[benzyl]$^+$	[(benzyl)Cr(CO)$_3$]$^+$
C(1)—C(2)	0.48	0.38
C(2)—C(3)	0.72	0.65
C(3)—C(4)	0.61	0.53
C(4)—C(5)	0.61	0.53
C(5)—C(6)	0.72	0.65
C(1)—C(7)	0.75	0.72

pected to lead to an increase in the π-bond order between C(1) and C(7) on complexation. As seen in Table 2, coordination to Cr(CO)$_3$ has only a minor effect on all the C—C π-bond orders. In fact a small decrease is universally observed, due to ligand to metal π-donation.

The fundamental cause of the changes in charge distribution and bond orders listed in Tables 1 and 2 becomes apparent from an examination of the molecular orbitals involved in the bonding. With the choice of axes employed in the calculations the metal (Cr^0-3d^6) d orbitals split up so that $3d_{xy}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ are formally each full, while $3d_{xz}$ and $3d_{yz}$ are vacant. Since the charge modifications on coordination were seen to occur largely via π-interactions we shall consider only the π-molecular orbitals of the benzyl cation. These are shown schematically in Fig. 1. The bonding orbital ψ_1 mixes with the chromium 4s and $4p_z$ orbitals, while ψ_2 and ψ_3 donate electrons into the $3d_{xz}$ and $3d_{yz}$ orbitals, respectively. On the other hand, the vacant non-bonding ψ_n has the correct symmetry for overlap with the filled chromium $3d_{x^2-y^2}$ orbital. This latter interaction is expected to lead to strong metal—ligand back donation. In

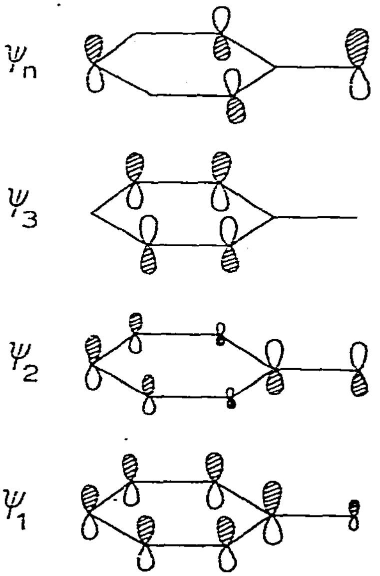


Fig. 1. π-Molecular orbitals for the benzyl cation.

fact, our calculations indicate that ca. 75 percent of the $d_{x^2-y^2}$ electron density is transferred to the benzyl ring in this way. The C(7) atom is the most strongly affected since ψ_n has a high location on this site (62%) as shown in Fig. 1. The remainder of this back donation occurs almost equally to C(2), C(4), and C(6), thereby neatly explaining the ring charge distribution in the benzyl complex (Table 1).

The above stabilization mechanism resembles a neighbouring group interaction. However, it does not involve specific bond formation betweeen the metal and C(7), but rather overlap with the benzyl ring as a whole. The absence of any significant changes in the C—C π-bond orders on complexation (Table 2) is also expected from the above interaction since ψ_n is non-bonding.

In view of this strong back bonding which gives a large metal—C(7) interaction, and the known structures of related ferrocenyl carbonium ions [13,14] and a tricarbonyl (fulvene) complex [15], it seemed probable that bending of the C(7) atom towards the chromium might occur in the present benzyl complex (I), as suggested recently by Hoffmann [16] for the corresponding iron species. The present calculations employing C(7)—ring angles between 0° and 60° in fact show that the most favourable geometry has a bending of ca. 40°. This configuration was more stable than the planar structure by ca. 150 kJ mol^{-1}. In contrast any bending away from a planar geometry for the free benzyl cation was energetically unfavourable.

It is interesting that the calculated bending angle of 40° for I is similar to the dihedral angles found for the ferrocenyl carbonium ions [13,14] and tricarbonyl-(diphenylfulvene) chromium [15]. With this minimised energy structure it is found that all seven carbon atoms of the benzyl cation are equidistant from the metal.

Finally, our calculations on I allow further comment concerning the general problem of the nature of the bonding between $Cr(CO)_3$ and π-hydrocarbons. As well as the back-bonding behaviour described above, the $Cr(CO)_3$ unit has been long known to have the ability to behave as an electron-withdrawing substituent. On the basis of reactivity patterns [17], dipole moment data [18], and the close similarity of the pK_a's of *p*-nitrophenyl- and -chromium tricarbonyl complexed phenylacetic acids [17a], $Cr(CO)_3$ is regarded as having a similar electron-withdrawing effect to that of a *p*-nitro group. However, the manner in which electron withdrawal is achieved is not fully understood and will depend on the nature of the π-hydrocarbon.

For the present $[(\text{benzyl})Cr(CO)_3]^+$ complex, the results indicate that electron withdrawal occurs primarily from the ring σ-orbitals (0.59 electrons from the seven carbon atoms). This is more than counterbalanced by the stabilizing back donation of 0.64 electrons into the ring π-system. After consideration of the ring hydrogens, a net gain of 0.21 electrons occurs for the benzyl ligand as a whole. These observations are similar to previous calculations [19] on the isoelectronic tropylium complex cation $[(C_7H_7)Cr(CO)_3]^+$ in which electron withdrawal (0.8 electrons) again arises from the ring σ-framework, but in this case significantly outweighs the donation (0.42 electrons) into the π-system.

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