# Relative Energies of the Ground and Core Hole States of the 1-Propyl and 2-Norbornyl Carbocations

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*Summary* Non-empirical LCAO MO SCF calculations on the ground state and localized $C_{1s}$ hole states of 1-propyl and 2-norbornyl carbocations have been carried out at the STO·4·31G level employing optimised geometries; the energetic preferences of the core ionized species are found to magnify energy differences which are small for the ground-state system.

It has become increasingly apparent over the past few years that electronic reorganizations accompanying core ionizations can substantially modify potential energy surfaces with respect to the ground state.[1] Despite the fact, therefore, that core electrons contribute insignificantly to bonding, core ionization is sufficiently strong a perturbation as far as the valence electrons are concerned to provide a monitor of overall valence electron distributions. One manifestation of the changes in potential energy surface consequent on core ionization is the recent observation of vibrational fine structure accompanying core ionization in simple molecules.[2] A particularly striking example of the changes in bonding accompanying core ionization arises for hydrogen-bonded dimers which we have recently investigated in some detail.[3] Thus for the water dimer removal of a core electron from the monomer providing the hydrogen for the hydrogen bond increases the hydrogen-bond strength compared with the ground-state system by some 40 kcal mol$^{-1}$. Core ionization can, therefore, considerably enhance comparatively weak interactions in appropriate systems and hence magnify energy differences which may be quite small for the ground-state system.

The electronic structure of isomeric classical and non-classical carbocations constitutes an area of intense research activity on both an experimental and a theoretical front[4] and it is interesting that the available evidence for the 1-propyl[5] and 2-norbornyl systems[6] indicates that for the isolated systems the energy differences between classical and non-classical formulations are extremely small. In the particular case of the 1-propyl cation for example the energy difference between the extended-chain and methyl-bridged formulations is computed to be 0·7 kcal mol$^{-1}$ (4·31G level), whilst the recent extensive study of Allen and Goetz[7] on the 2-norbornyl system indicates that the energy difference for the classical and non-classical formulations is $<$ 0·2 kcal mol$^{-1}$.

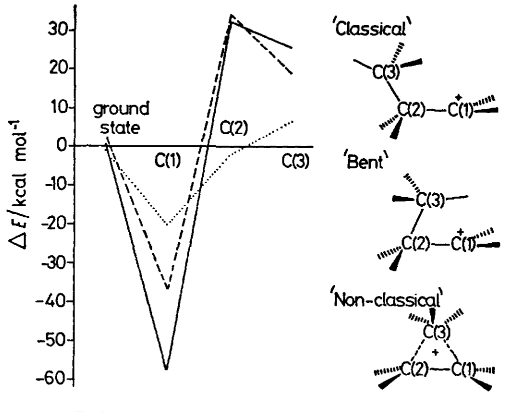

Figure 1. Relative energy-differences for the 1-propyl cation, (a) between 'classical' and 'bent' species; (b) between 'bent' and 'non-classical' forms; (c) between 'classical' and 'non-classical' forms. The three species 'classical,' 'bent,' and 'non-classical' correspond to Pople's (ref. 5) methyl-staggered 1-propyl, methyl-eclipsed 1-propyl, and corner-protonated cyclopropane respectively.

We now indicate how detailed theoretical consideration of the ground and hole states provides considerable insight into structure and bonding in these systems. Non-empirical LCAO MO SCF computations on the ground-state and localized $C_{1s}$ hole states have been carried out at the STO-4·31G level employing appropriate optimized geometries.[5,7] Previous studies have indicated that differences in core binding and relaxation energies are well described at this level.[8]

We have previously commented on the characteristic nature of the core level spectra of carbocations in general[9] and we consider here the energetic preferences for the core ionized species.

As a starting point, we consider the 1-propyl cation, Figure 1. The dotted line shows the relative energy-difference between the 'classical' (extended chain) and 'bent' species, and it is apparent that creation of a core-hole, and hence increased valence electron demand, on C(1) favours the bent form by *ca.* 20 kcal mol$^{-1}$. By contrast, creating a core-hole on C(3) slightly favours the classical form, which again may be taken as evidence for slight electronic interaction between C(3) and C(1) in the bent form of the 1-propyl cation. For the creation of a core-hole on C(2), however, the energetic preference essentially remains the same. Considering now the 'bent' and 'non-classical' (corner-protonated cyclopropane, or methyl-bridging propyl cation) forms, from the results indicated by the dashed line, it is apparent that the creation of a core hole on C(1) markedly favours participation with C(3), whereas a core-hole on the other carbon atoms obviates such an effect, favouring instead the 'bent' structure. The solid line, pertaining to the energy difference between the 'classical' and 'non-classical' form of the 1-propyl cation is effectively the sum of the former two lines, and shows that creation of a core-hole at C(1) now greatly favours the latter (by *ca.* 57 kcal mol$^{-1}$), whereas a core-hole on either C(2) or C(3) favours the 'classical' structure by *ca.* 32 and 25 kcal mol$^{-1}$, respectively.

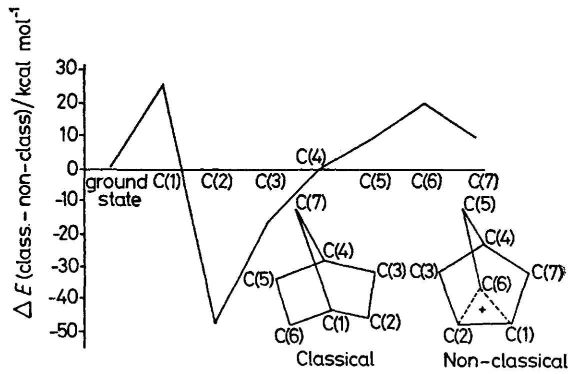

Figure 2. Relative energy-differences between the classical and non-classical forms of the 2-norbornyl cation.

Similar trends are shown in Figure 2, for the 2-norbornyl system. Thus, a core-hole on C(2) enhances participation, with the result that the non-classical species is favoured by *ca.* 48 kcal mol$^{-1}$. On the other hand, creation of a core-hole at C(1) or C(6) [*i.e.*, atoms which in the non-classical case are donors to C(2)] leads to the classical cation being favoured by *ca.* 25 and 19 cal mol$^{-1}$, respectively.

The manifestation of these results is that the core-hole state spectra are highly characteristic for the isomeric species and differ quite significantly for systems which on an absolute energy scale are quite closely similar.

The lifetimes of the hole states are typically expected to be in the range $10^{-13}$—$10^{-14}$ s and the manifestation of the substantial changes in potential energy surface in going from the ground state to core-hole state, therefore, is likely to be small asymmetries of the core-hole state spectra arising from vibrational excitation accompanying core ionization. Such excitations are difficult to detect even for small molecules studied in the gas phase and for carbocations studied in the condensed phase would almost certainly remain undetected.

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