

On the rigidity of planar tricoordinate carbon

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A linear relationship has been found between the computed out-of-plane bending force constants of the methylene group and the total charge transfer from X to CH₂ for the series XCH₂⁺ (X = H, CH₃, NH₂, OH, F) and CH₂=X (X = O, NH, CH₂, S). As the electron-withdrawing power of X increases, out-of-plane bending becomes more difficult in all cases. Two complementary interpretations of this result are proposed.

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On a trouvé une relation linéaire entre la vibration de déformation angulaire hors plan du groupe méthylène et la charge de transfert totale de X à CH₂ pour une série de XCH₂⁺ (X = H, CH₃, NH₂, OH, F) et de CH₂=X (X = O, NH, CH₂, S). A mesure que le pouvoir électroaffinitaire de X augmente, la vibration de déformation angulaire hors plan devient plus difficile et ce dans tous les cas. On propose deux interprétations complémentaires pour expliquer ce résultat.

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Introduction

In general, carbonium ions¹ and carbanions are characterized, respectively, by trigonal planar (2) and pyramidal (3) configurations at carbon. Therefore, substitution at a carbanionic centre can be expected to affect both its stability and its stereochemical capabilities (*e.g.*, the barrier to pyramidal inversion), but in the case of a carbonium ion, only the first of these effects would appear to be susceptible to ready experimental observation. Thus, although many physical and spectroscopic properties of carbonium ions have been described (1, 4), to our knowledge there has been no systematic determination of the rigidity or 'degree of planarity' (*i.e.*, ease of out-of-plane bending) of any series of carbonium ions.

It is reasonable to assume that the degree of planarity of a planar species should be subject to recognizable substituent effects because, from a theoretical standpoint, the single well potential associated with the distortion from planarity of a carbonium ion is just a special case of the double well potential characteristic of carbanions (3). In the case of carbanions, it is well established that relative stabilization of a planar conformation occurs as the substituents are made larger (*i.e.*, steric effects), electron-delocalizing (*i.e.*, conjugative effects), and electron-releasing

(*i.e.*, inductive effects). The inductive effect associated with an electron-withdrawing substituent causes relative stabilization of a non-planar conformation. If these same effects were operative upon the degree of planarity of carbonium ions then, depending on the balance between an electron-withdrawing inductive effect on the one hand, and a combination of steric, conjugative, and electron-releasing inductive effects on the other hand, bending of the carbonium ion might become facilitated.

The present work was undertaken to assess the balance of effects just mentioned, by a theoretical study of the out-of-plane bending force constants of the series of cations XCH₂⁺ (X = H, CH₃, OH, NH₂, F). In the case of HOCH₂⁺, the force constants were calculated for both the all planar energy minimum **1** (5) and the conformation **2**, in which the π -conjugative effect is substantially reduced. The results of the computations were rather unexpected, and the work was, therefore, extended to the neutral molecules CH₂=O, CH₂=NH, CH₂=CH₂, and CH₂=S.



1

2

Calculations

Force constants were computed by the force method (6). The forces, *i.e.*, the negative of the

¹This terminology refers to trivalent ('classical') carbonium ions. See ref. 1.

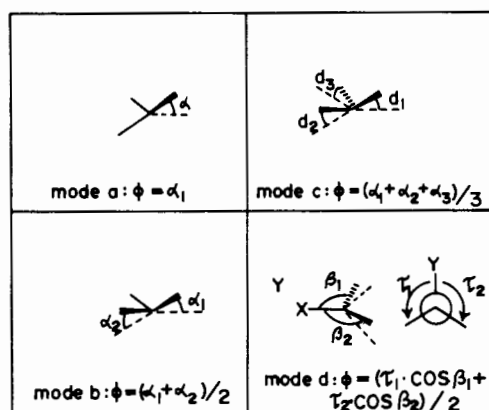
TABLE I. Charge transfer^a and out-of-plane bending force constants^b of the carbonium ions X-CH₂⁺^c

X	π (X \rightarrow CH ₂ ⁺)	σ (X \rightarrow CH ₂ ⁺)	Total (X \rightarrow CH ₂ ⁺)	k
H		0.344	0.344	0.418(0.431)
CH ₃	0.135	0.143	0.278	0.441(0.440)
NH ₂	0.517	-0.291	0.226	0.438
OH ^d	0.379	-0.354	0.025	0.481(0.465)
	0.263	-0.300	-0.037	0.567
F	0.222	-0.420	-0.198	0.508

^aIn units of electrons.^bIn units of mdyn Å.^cThe following geometrical parameters were employed:

CH₃⁺: $r_{CH} = 1.077$ Å, $\angle HCH = 120^\circ$
 CH₃CH₂⁺: $r_{CH}(CH_3) = 1.1$ Å, $r_{CH}(CH_2^+) = 1.077$ Å, $r_{CC} = 1.44$ Å, $\angle HC^+C = 121^\circ$,
 $\angle HCC = 109.5^\circ$

NH₂CH₂⁺: $r_{CH} = 1.103$ Å, $r_{NH} = 1.038$ Å, $r_{CN} = 1.292$ Å, $\angle NCH = \angle CNH = 120^\circ$
 HOCH₂⁺: $r_{CH} = 1.114$ Å, $r_{OH} = 1.003$ Å, $r_{CO} = 1.252$ Å, $\angle COH = 114.7^\circ$, $\angle HCO(HC$ *syn*
 to OH) = 123° , $\angle HCO(HC$ *anti* to OH) = 116.4°
 FCH₂⁺: $r_{CH} = 1.127$ Å, $r_{CF} = 1.265$ Å, $\angle FCH = 120^\circ$.

^dThe first row refers to computations on conformation 1, and the second row to computations on conformation 2.FIG. 1. Possible choices for the out-of-plane bending coordinate (ϕ) for a tricoordinate species.

first derivatives of the energy with respect to the nuclear coordinates, are computed analytically. These are then differentiated numerically to obtain the force constants. The SCF computations were performed using the Gaussian 70 programme system (7) and the standard 4-31G basis set (8). The forces and force constants were calculated using a series of programmes written in this laboratory (9). Various test systems have shown that the 4-31G basis set gives force constants that agree well with experimental and other theoretical work (10).

There are a number of choices for the out-of-plane bending coordinate ϕ . These are illustrated in Fig. 1, as follows: (a) mode a, in which

one atom moves out of the plane; (b) mode b, in which two atoms move out of the plane; (c) mode c, in which three atoms move out of the plane; (d) mode d, in which the out-of-plane motion is specified in terms of the dihedral angles. With the indicated normalization of the out-of-plane bending coordinate, each of these modes leads to the same harmonic force constant.² For convenience, mode d was chosen.

The bending force constants of CH₃⁺, CH₃CH₂⁺, and HOCH₂⁺ were also calculated, using mode b, by fitting computed energies to a quadratic equation of the internal coordinate. The energies were obtained, using the IBMOL 4 programme system (11), and a double zeta basis set of contracted gaussian functions ($13^s7^p/4^s2^p$ for C and O (12), and $4^s/2^s$ for H (13)).

Results and Discussion

Table 1 summarizes the results obtained for the cations XCH₂⁺. The last column shows the computed out-of-plane bending force constants obtained by the force method; the numbers in parentheses are the values obtained by fitting a quadratic equation to the IBMOL 4 computed energies, and it is seen that the same trends are predicted by both methods.

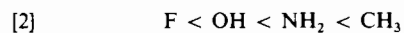
The rigidities of these cations are found to be:



²However, the quartic force constants will depend upon the choice of coordinate.

This finding is just the opposite of that expected by the assumption that increasing the ligand electronegativity should have led to a decrease in the rigidity of the carbonium ion centre, except for the relative positions of CH_3CH_2^+ and CH_3^+ .³

It follows that inductive effects are not a dominant factor in determining the ease of out-of-plane bending of these carbonium ions. Although none of the substituents shown in eq. 1 is particularly bulky, consideration of A values (15) as a measure of their steric effects suggests that these should increase in the order



Clearly, the trend seen in eq. 1 is also not compatible with an assumption that steric effects are important in determining the flexibility of these carbonium ions. Therefore, it seemed to follow that the π -conjugative effect of X must be the dominant factor which decides the orderings of eq. 1. According to the classical view, p_π - p_π conjugation is associated with increasing stability of planar configurations at the interacting centres. This leads to the unreasonable conclusion that in the present system the extent of such conjugation increases in the direction



To take this point further, the out-of-plane bending force constant was calculated for conformation **2** of HOCH_2^+ . Since the degree of π -conjugation in **2** must be less than in **1**, the bending force constant of **2** should have been smaller than that of **1**. However, as seen in Table 1, this is not the case. The bending force constants of **1** and **2** are 0.481 and 0.567 mdy \AA , respectively.

Thus none of the classical effects which are commonly considered to influence molecular structure can be responsible for our findings. To gain additional insight into the problem, the amount of charge transfer from X ($X = \text{H}$,

³ This presumes that methyl is to be regarded as an electron-releasing substituent (however, *vide infra*). It should be noted that the force constant computed for ethylcarbonium ion in the present work refers to out-of-plane bending of a trigonally planar carbonium ion centre. Although the CH_2^+ group is slightly non-planar in the fully optimized geometry of the classical structure of ethylcarbonium ion (14), the average structure of the CH_2^+ group is planar because of the very low barrier to internal rotation.

CH_3 , NH_2 , OH , F) to the CH_2^+ moiety was computed, based upon the Mulliken population analysis (see columns 1-3 of Table 1).⁴ This quantity can be partitioned into the π and σ contributions (5). The former is the gross charge of the p -orbital, and will be zero when there is no π -type charge delocalization between X and CH_2^+ . The total charge transfer in XCH_2^+ is the sum of the gross atomic charges on the CH_2^+ group minus seven.

The magnitude of the π -charge transfer may be considered as a measure of the extent of π -conjugation. As was already deduced from the computations on **1** and **2**, it is evident that the amount of π -conjugation does not correlate with the rigidity of the carbonium ion centre. On the other hand, the σ -charge transfer and, even more strikingly, the total charge transfer correlate well with the out-of-plane bending force constants. This means that, as the electron-withdrawing power of the substituent increases, the out-of-plane bending of the carbonium ion becomes more difficult.⁵

This result demonstrates that it is not valid to assume that substituent effects that operate upon barriers to pyramidal inversion of carbanions and on the rigidity of carbonium ions are the same. An electron-withdrawing substituent causes relative stabilization of the geometry of the energy minimum, regardless of whether its conformation is pyramidal or planar.

Our results can be rationalized in two ways. In terms of the Walsh-Mulliken model (18), the pyramidality of CH_3^- can be regarded as the result of electron occupation of the vacant p -orbital of CH_3^+ , which is planar. This model predicts that π -electron transfer from X to CH_2^+ in XCH_2^+ will facilitate the bending of the carbonium ion centre or, conversely, that the carbonium ion will become more rigid as π -bonding becomes less effective. This is the

⁴The discussion which follows is subject to the usual caveats concerning the basis set dependence of the Mulliken population analysis (16). However, our argument is based upon trends rather than absolute magnitudes and, in any event, all computations were performed with the same basis set.

⁵It will be noted that, relative to hydrogen, methyl is not electron-releasing but electron-withdrawing because of the combination of its σ and π effects. The polarizable nature of this group (17) allows it to stabilize both cationic and anionic centres.

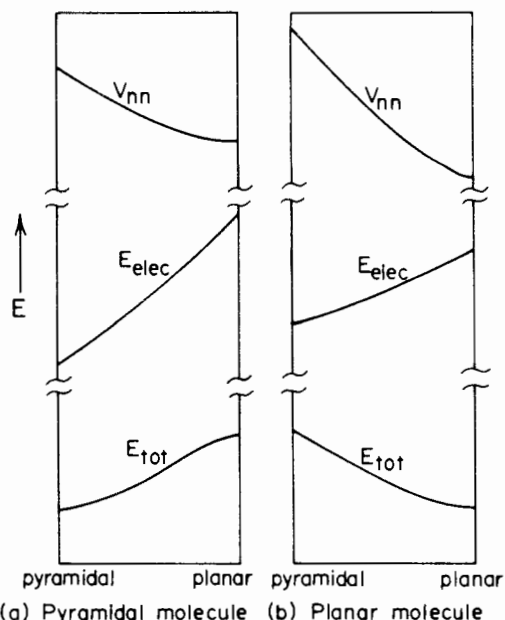


FIG. 2. Schematic diagrams showing the total energy and its nuclear and electronic components for pyramidal (a) and planar (b) species.

observation in the series FCH_2^+ , HOCH_2^+ (1), and H_2NCH_2^+ , and it accounts for the difference between the two conformations of HOCH_2^+ . The same reasoning may be applied to the behaviour of carbanions. In XCH_2^- , conjugation results in π -electron transfer from $^-\text{CH}_2$ to X, and it leads to a decrease in the pyramidity of the carbanionic centre (19). What is significant about this model is that the effects of π -electron transfer upon the geometries of adjacent carbonium ions and carbanions are predicted correctly, in contrast to the classical view which predicts incorrectly that both systems become more planar with increasing π -electron transfer.⁶

On the other hand, we have found that our results are better correlated with the total charge transfer than either the σ - or π -effects alone. It is appropriate, therefore, to search for a rationalization of the results which focusses upon the whole system and not just one of the interactions present in this system. Such a rationalization can be provided by making use

⁶The argument just presented is based upon comments communicated to us independently by Professors W. J. Hehre (personal communication), F. Bernardi and N. D. Epitotis (to be published) and L. C. Allen (20). We thank these workers for drawing our attention to the predictive utility of the Walsh-Mulliken model.

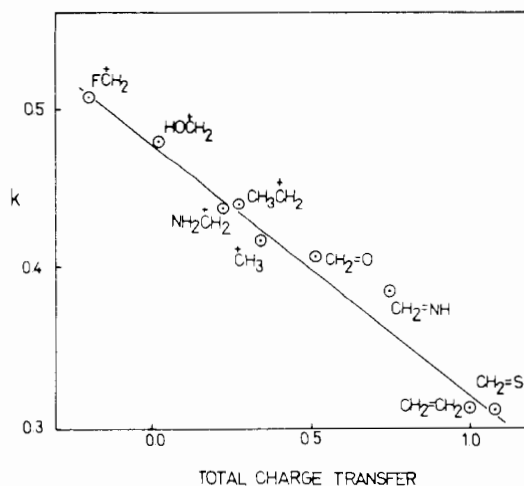


FIG. 3. A plot of total charge transfer versus out-of-plane bending force constant for the cations XCH_2^+ and the molecules CH_2X .

of energy component analysis (21). Figure 2a shows the behaviour of the electronic and nuclear components of the total energy for a pyramidal molecule. In this case, the total energy is dominated by the electronic component, so that electron pair repulsion considerations (22) (which are part of the electronic component) correctly simulate the behaviour of the total energy. However, as seen in Fig. 2b, for a planar molecule it is the nuclear component which dominates. In terms of such an analysis, it is easy to understand why the removal of electronic charge from a carbonium ion centre will make this centre more rigid, because this increases further the dominance of the nuclear term.

The above arguments should be applicable not only to carbonium ions but to all systems which have trigonal planar geometry about a central atom, e.g., planar neutral molecules. The available experimental data support this view. Thus, the out-of-plane bending frequencies of $\text{CH}_2=\text{CH}_2$, $\text{CH}_2=\text{NH}$, and $\text{CH}_2=\text{O}$ are found at 949 cm^{-1} (23), 1120 or 1057 cm^{-1} (24), and 1167 cm^{-1} (25), respectively. Table 2 summarizes the computed charge transfer⁷ and bending force constants of the neutral molecules $\text{CH}_2=\text{X}$ ($\text{X}=\text{O}$, NH , CH_2 , S). This table again shows the correlation between out-of-plane bending force constants and the total charge transfer.

⁷The charge transfer was calculated by treating $\text{CH}_2=\text{X}$ as $^+\text{CH}_2-\text{X}^-$.

TABLE 2. Charge transfer^a and out-of-plane bending force constants^b of the neutral molecules CH₂=X^c

X	π (X \rightarrow CH ₂ ⁺)	σ (X \rightarrow CH ₂ ⁺)	Total	<i>k</i>
O	0.734	-0.220	0.514	0.408
NH	0.885	-0.136	0.749	0.384
CH ₂	1.0	0.0	1.0	0.314
S	0.831	0.244	1.08	0.313

^aIn units of electrons. The charge transfer was calculated by assuming that these species consist of carbonium ions bearing negatively charged substituents, *i.e.*, ⁺CH₂-O⁻, ⁺CH₂-NH⁻, ⁺CH₂-CH₂⁻, ⁺CH₂-S⁻.

^bIn units of mdyn Å.

^cThe following geometrical parameters were employed:

CH₂O: $r_{CH} = 1.09$ Å, $r_{CO} = 1.21$ Å, $\angle OCH = 120^\circ$

C₂H₂: $r_{CH} = 1.086$ Å, $r_{CC} = 1.337$ Å, $\angle CCH = 121.35^\circ$

CH₂S: $r_{CH} = 1.09$ Å, $r_{CS} = 1.6375$ Å, $\angle SCH = 120^\circ$

CH₂NH: $r_{CH}(CH_{syn} \text{ to } NH) = 1.091$ Å, $r_{CH}(CH_{anti} \text{ to } NH) = 1.089$ Å, $r_{NH} = 1.048$ Å,

$r_{CN} = 1.273$ Å, $\angle CNH = 109.1^\circ$, $\angle HCN(CH_{syn} \text{ to } NH) = 125.4^\circ$,

$\angle HCN(CH_{anti} \text{ to } NH) = 119.1^\circ$.

Figure 3 plots the computed bending force constants *vs.* the total charge transfer for all of the systems studied in the present work. The linear relationship observed in this figure may be taken as evidence that effects of substituents upon the rigidities of carbonium ions and planar neutral molecules are the same.

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