Tetrahedron Vol. 33, pp. 2267 to 2270 Pergamon Press 1977 Printed in Great Britain

ON THE INVERSION BARRIERS OF PYRAMIDAL CARBANIONS

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(*Received in UK 7 January 1977; Accepted for publication 9 March 1977*)

Abstract—A simple MO model is used to explain the trends exhibited by inversion barriers of pyramidal carbanions upon variation of its substituents. Free carbanions as well as carbanions solvated by H_2O molecules are considered.

Elucidation of the structure of carbanions by MO methods has been the subject of several recent reports.[1-5] Carbanions possessing substituents capable of conjugative stabilization exhibit complex energy surfaces. The absolute minimum of the surface corresponds to a planar species in which full overlap between a p orbital on carbon and the π-system of the substituent occurs. A pyramidal carbanion where the lone pair on carbon conjugates with the substituent, may or may not be present depending on other groups attached to the C atom. Other minima of considerably higher energy are present which correspond to pyramidal anions where conjugation between the carbon lone pair and the substituent is avoided by a 90° rotation around the C-substituent bond. Carbanions possessing intrinsically non-conjugating substituents exhibit a single minimum corresponding to a pyramidal species.

Inversion barriers have been calculated for pyramidal carbanions.[11-14] Contrary to related experimental work on substituted amines,[6,15] their magnitude does not increase with increasing electron-withdrawing power of the substituent.[16] When a CHO substituent replaces a hydrogen in Me anion to form a pyramidal species, the inversion barrier, as calculated using *ab initio* methods, decreases.[11,14]

In this work a simple MO picture is used to examine this problem.

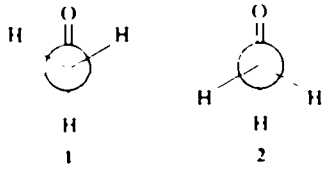
METHODS

Calculations were carried out on pyramidal and planar configurations of substituted Me anions using the CNDO/2 method[19] with full geometry optimization.[20] This approach has been proven successful in other studies of carbanions.[21] Only the conformers where the carbanionic center does not conjugate with the substituent were studied in the case of formylmethyl anion.

RESULTS AND DISCUSSION

Comparison was made of our CNDO/2 results with *ab initio* calculations available from the literature. Although the magnitude of the inversion barriers calculated with *ab initio* methods have been shown to depend strongly on the size of the basis set, the inclusion of polarization functions and the Slater exponents used,[3,21] trends are reliable when a single basis set and Slater exponent set are used throughout the series.

The results in Table 1 show that the inversion barriers calculated with the CNDO/2 method parallel *ab initio* results using an STO-3G basis set. Other effects also parallel *ab initio* results: the relative stabilities of **1** and **2** are correctly predicted, and upon transformation of the pyramidal anion into a planar one, the C–H bond distance decreases, the population of the carbon 2p orbital increases while that of the carbon 2s orbital decreases and the net charge on carbon increases while that on hydrogen decreases[3] (Table 2 and discussion below). Finally, experimental results indicate that the inversion barrier of Me carbanion is slightly higher than that of ammonia,[22] and that the inversion barrier of oxonium ion is very small.[23] These trends are also reproduced by our calculations (Table 1). These successful comparisons lead us to believe that our CNDO/2 calculations are reliable.



1 **2**

Inversion barriers. The inversion barriers of AH_3 molecules were shown to be governed by the change in energy of the highest occupied MO (HOMO) during the inversion process, made possible by its strong interaction with the lowest unoccupied MO (LUMO).[24,25] The same arguments apply to the case of the Me anion. Figure 1 shows the orbitals for planar and pyramidal Me anions calculated by the CNDO/2 method.

The energy lowering of the 2p orbital (interaction energy) caused by its interaction with one σ^*_H orbital is given by first order perturbation theory as

$$\Delta E = (k \cdot c \cdot S_{2p_C,1s_H})^2/\Delta E_{5,4} \qquad (1)$$

where c is the coefficient of the H atoms in orbital 4 (Fig. 1), $\Delta E_{5,4}$ the energy difference between orbitals 5 and 4, and $S_{2p_C,1s_H}$ the overlap integral between carbon 2p and hydrogen 1s orbitals in the pyramidal species.[24]

In order to allow a direct comparison between the results on carbanions and those on ammonia and the oxonium cation, a value was assigned to k according to the equation:

$$k = 1.75(H_{ii} + H_{jj})/2 \qquad (2)$$

where H_{ii} and H_{jj} are taken as average valence state ionization potentials of 1s orbital of hydrogen and 2p orbitals of carbon, nitrogen and oxygen respectively.[26] The results (Table 1) show a remarkable parallelism between inversion barriers and interaction energies (Fig. 2, correlation coefficient = 0.968).

It was argued that the electronegativity of a substituent in an AH_3 molecule, to the extent that it affects

Table 1. Barriers for inversion and interaction energies

Species	E_{inv}[a] CNDO/2	E_{inv}[a,b] STO-3G	$\Delta E_{i,j}$[c]	$\Delta E'$
$^{\ominus}OH_3$	3.4		0.922	0.090
CH_2CH_3	6.7		0.670	0.127
$CH_3{\cdot}2H_2O$	8.5		0.512	0.126
$CH_2CHO{\cdot}3H_2O$	12.5		0.536	0.157
CH_2CHO	14.7	18.99	0.683	0.144
NH_3	16.0		0.792	0.155
CH_3	19.2	28.85	0.691	0.154
CH_2OH	20.3		0.642	0.146
CH_2F	32.6	36.78	0.635	0.191
$CH(OH)F$	36.8		0.606	0.236
CHF_2	53.3		0.592	0.325

[a] In kcal/mol.
[b] Refs. 11 and 14.
[c] In Hartrees. Refer to eqns 1 and 2.

Table 2. Force constants and population changes during inversion

Anion	ΔC_{α}	ΔC_{p_z}	$\Delta\delta_H$	$\Delta\delta_C$	k_{α}[a]
CH_2CH_3	−0.221	0.232	0.026	−0.013	2.2
CH_2CHO	−0.288	0.368	0.030	−0.056	2.0
CH_3	−0.334	0.478	0.036	−0.109	3.2[b]
CH_2F	−0.418	0.615	0.064	−0.136	4.4
CHF_2	−0.512	0.706	0.112	−0.164	5.4

[a] In mdyn/A.
[b] For comparison, a value of 2.0 mdyn/A was obtained in *ab initio* calculations with (8s; 10s, 6p, 1d) basis set.[3]

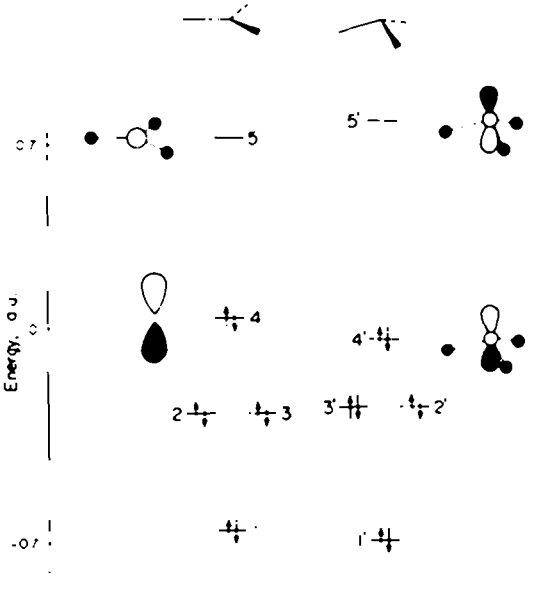


Fig. 1. Molecular orbitals involved in the inversion process of methyl carbanion.

the energy of σ^*_H but not that of $2p_A$, should influence the height of the barrier. An increase in electronegativity of the substituent should bring a decrease in the energy of σ^*_H, an increase in the σ^*_H–$2p_A$ interaction and thus an increase in the inversion barrier.[10,22] The present data (Table 1) point out the danger of considering only the σ^*_H–$2p_C$ energy difference in carbanions.

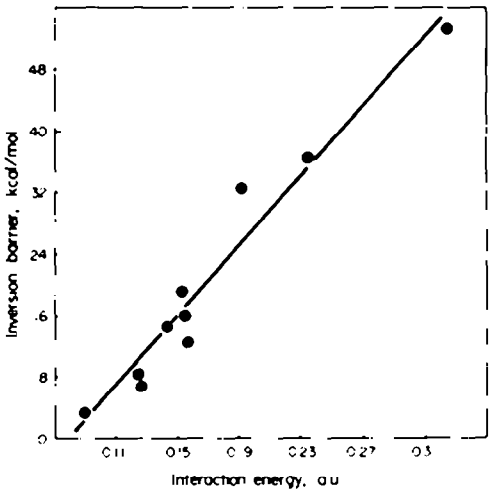


Fig. 2. Correlation between inversion barriers and energy of interaction between HOMO and LUMO.

The effect of the substituent on the σ^*_{CH}–$2p_C$ interaction can be studied in terms of intuitively simple concepts such as electronegativity and orbital overlap using the simplified PMO scheme of Fig. 3.

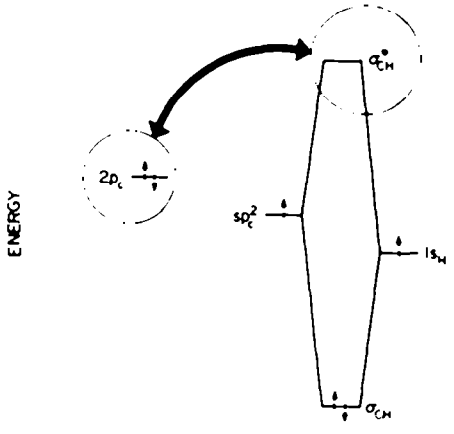


Fig. 3. PMO scheme for the $2p_C$–σ^*_H interaction, shown as a double-headed arrow.

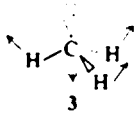
A substituent can be pictured to interact with the $2p_C$, sp^2_C and $1s_H$ orbitals. In the absence of overlap effects the more electronegative the substituent, the smaller the sp^2_C–$1s_H$ interaction and hence the lower the energy of σ^*_H on one hand, and the higher the energy of $2p_C$ on the other (Fig. 3). Consequently, the σ^*_H–$2p_C$ interaction and hence the inversion barrier should increase.

In cases where the substituents, X, are CH_3, CHO, OH and F, the C–X and H–X overlaps are comparable (the C–X and H–X distances vary by less than 5%) and the inversion barriers follow the trends of electronegativities: $CH_2CH_3 < CH_2CHO < CH_2OH < CH_2F < CHF(OH) < CHF_2$. In Me carbanion however, the distances are substantially shorter (C–H = 1.11 Å compared to C–X ≅ 1.38 Å and H–H = 1.80 Å compared to H–X ≅ 1.17 Å), the overlap consequently is greater and the barrier higher than expected on the sole basis of electronegativity effects.

The preponderant role of the $2p_C$ orbital can also be

assessed through the population changes which occur upon inversion. Thus, considering the transformation of orbital 4' into 4 (Fig. 1), a shift of electron density from hydrogen to carbon and from carbon 2s to carbon 2p orbital is predicted. These trends are borne out by the data in Table 2. In fact, the anions which show higher interaction energies (see Table 1) show also higher degrees of electron density shifts.

Force constants. An indication of the height of the inversion barrier may be sought in one of the two A_1-symmetry normal modes of vibration (or an analogous mode in substituted Me anions where C_s symmetry is no longer present), as shown for Me anion in 3.[17] The



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behaviour of the total energy of the molecule with respect to this vibration is shown in Fig. 4a. The vibration involves the movement of all the atoms; however, because of the difference in mass between hydrogen and carbon (or other heavy atoms in substituted anions), a wagging motion of one H atom may serve as a crude approximation. We have assumed this wagging motion to behave as a harmonic oscillator and have calculated the force constants accordingly. Table 2 shows that the force constants are proportional to the inversion barriers and thus provide another useful criterion for assessing the configurational stability of an AH_3 species.

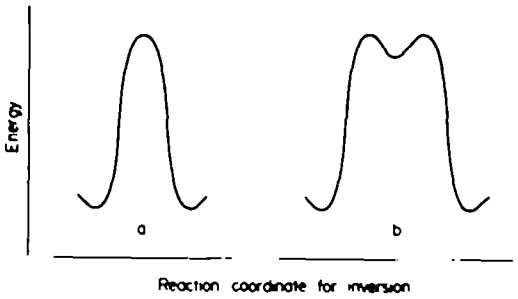
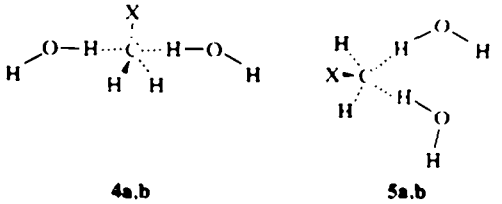


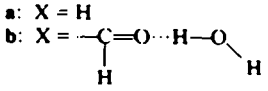
Fig. 4. Energy profiles for the inversion process of an isolated carbanion (a) and a solvated one (b).

Solvation studies. In order to assess the influence of solvent on the inversion barriers of carbanions, the solvation of planar and pyramidal Me anions by water molecules was studied using **4** and **5** as models for the first solvation shells.[15] The inversion process is more complex than in the case of isolated carbanions since the solvated planar carbanion represents a minimum in the energy profile (Fig. 4b). The difference in energy between



4a,b **5a,b**

a: X = H

b: X = 

5 and **4** no longer represents exactly the inversion barrier; however, since the pyramidal to planar transformation is endothermic, the transition state will closely resemble **4** and thus the inversion barrier will not differ substantially from E(**4**) − E(**5**).[28]

The fact that the points for the solvated species fall on the correlation line of Fig. 2, shows that solvation effects may be interpreted on the same basis as substituent effects, where the H_2O molecules are treated as additional substituents. The interaction between $2p_C$ and σ^*_{OH} of H_2O lowers the energy of $2p_C$, decreases the $2p_C$–σ^*_{CH} interaction and hence lowers the barriers for inversion.

Solvent effects can also be explained on purely electrostatic basis, taking into account the predominant role of the $2p_C$–σ^*_{CH} interaction. The central C atom is the origin of most of the solvation energy and a shift of electron density in its direction occurs as the anion becomes planar (Table 1). Hence, solvation of the (nearly) planar transition state is more important than that of the pyramidal species and hence the barrier for inversion decreases upon solvation.

CONCLUSION

The trends exhibited by inversion barriers of isolated and solvated pyramidal carbanions upon variation of its substituents follow qualitative ideas on electronegativity and overlap and on force constants and may be interpreted in terms of the interaction between the lone pair on carbon and the σ^*_{CH} orbital. The trends are reliably reproduced by CNDO/2 calculations with geometry optimization.

Acknowledgements—The author wishes to express his gratitude to Prof. H. Dahn for his encouragement and advice. The finantial support given to Prof. Dahn by the Fonds National Suisse pour la Recherche Scientifique (Project No. 2.772.72) is gratefully acknowledged.

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