Short Communication

The Instability of the Planar Structure of Carbanion ⊖ :CH₂–CN

Paul G. Mezey

Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0

Michael A. Robb

Department of Chemistry, Queen Elizabeth College, University of London, London, England

Keith Yates and Imre G. Csizmadia

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 1A1

Ab initio SCF calculations using uniform quality extended basis set supplemented with polarization functions predict a slightly pyramidal carbanion centre in ⊖:CH₂–C≡N. This finding is in contrast to the usual finding of planar geometry of carbanion centres generated next to other conjugative groups. Although the predicted barrier to pyramidal inversion is very small (~0.1 kcal/mole) it is estimated that correlation energy contributions, neglected in any SCF calculations, may be too small to remove the barrier. The present results confirm earlier experimental findings that counter-ion and solvent effects can have a dominant role in determining the geometry of this unusual ion in actual chemical systems.

Key words: Pyramidality of carbanions – Competitive inductive and conjugative effects – *Ab initio* calculations on carbanions

1. Introduction

Carbanions are pyramidal except when generated next to a group capable for conjugative stabilization that, in general, favours a *planar* carbanion centre. The conjugate base of acetaldehyde (I) and that of nitromethane (II) are well known examples for such planar carbanion structures [1, 2], although *ab initio* SCF MO calculations for II have indicated an extremely shallow potential along a pyramidal distortion coordinate [2].
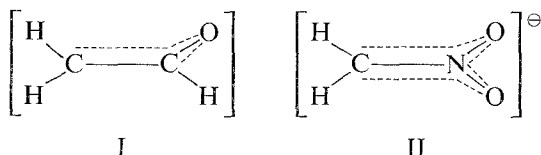
The –C≡N group is certainly capable of conjugative stabilization, the carbanion $^{\ominus}$:CH$_2$–C≡N exhibits some unexpected features. Extensive experimental studies [3, 4] on various addition reactions of M$^{\oplus}$:$^{\ominus}$CH$_2$CN systems in non-aqueous solvents such as THF gave no firm evidence as to the pyramidality or planarity of $^{\ominus}$:CH$_2$CN. Nevertheless, when M$^{\oplus}$ is Na$^{\oplus}$ or K$^{\oplus}$ a pyramidal carbanion structure appeared to be more likely [4].

2. Results and Discussion

We now wish to report the results obtained from a series of *ab initio* SCF calculations on the conjugate base of acetonitrile (III) that are markedly different from I and II. These results are in contradiction to the general rule of conjugative stabilization. The geometry of the carbanion centre in III is shown to be pyramidal corresponding to an equilibrium situation:

(III)
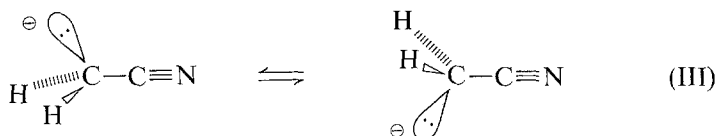
with the planar, fully conjugated system as transition state.

The calculations included two different minimum basis sets (3G and 4G expansions) [5] as well as a sesqui ($1\frac{1}{2}$) zeta (4-31G) [6] basis set and a Uniform Quality extended (5G) basis set [7, 8] in a sester ($2\frac{1}{2}$) zeta contraction, augmented with a set of polarization functions (p functions on both H and d functions on the carbanion carbon)[1].

The inversion coordinate (γ) is defined in Fig. 1. The points computed along γ were optimized with respect to all internal coordinates independent of γ. The
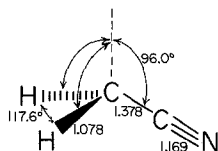

Fig. 1. Optimum geometry of $^{\ominus}$:CH$_2$–CN. Inversion coordinate γ is measured from a hypothetical pyramidal axis (HCH bond angle ϕ is varied independently of γ)

results are summarized in Fig. 2. It appears that the theoretical prediction for the optimum geometry of this particular ion is extremely sensitive to the size and the quality of the basis set chosen. While both 3G and 4G minimum basis sets predict pyramid structures as the most stable geometry with a 0.43 and 0.05 kcal/mole barrier height to inversion, respectively, the 3-31G basis calculation indicates a planar structure. Since in all our calculations negative HOMO orbital energies were obtained, the contradictory results could not be attributed to an artifact of unstable HOMO, often encountered in attempted minimum basis calculations on

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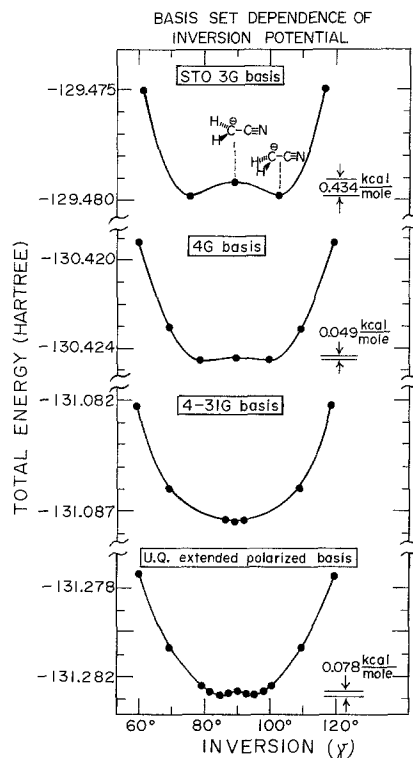[1]   Exponents for polarization functions are: $p(H) = 1.0000$, $d(C) = 0.7969$

Fig. 2. Inversion potential of $^{\ominus}$:CH$_2$–CN as calculated with various basis sets

negative ions. Nevertheless, the computed barriers in both minimum basis set calculations were extremely small and considering the given level of approximations no conclusions could be drawn from the first three calculations. For this reason we decided to carry out more accurate calculations using a large polarized basis set which was composed from carefully balanced [9, 10] Uniform Quality AO bases [7, 8]. The optimized geometry for $^{\ominus}$CH$_2$–CN is shown in Fig. 1.

The ion appears to be slightly pyramidal (out of plane angle $\Delta\gamma = 6°$) with a barrier of ~ 0.1 kcal/mole but one should interpret the results with some caution. Energy differences of this order are much too small to be regarded reliable on the one-determinant SCF level, even if one uses large polarized basis sets. It is conceivable that the correlation energy difference between the planar and pyramidal structures may exceed the 0.1 kcal/mole limit, provided that there are major differences in geometry and consequently in the wavefunction. According to rather reliable calculations on the CH$_3^-$ anion [11], however, inclusion of correlation contributions did not change the optimum out of plane angle γ by more than 0.5 degree; in spite of the fact that there were considerable geometry differences ($\Delta\gamma = 18°$) between the optimum pyramidal structure and the planar transition state. In the present case the overall geometry variation is much smaller (i.e. $\Delta\gamma = 6°$) and the MO coefficients show very little change only. Although one should not rely too heavily on such an analogy, this comparison lends support to the present SCF result with the large polarized basis.

On the other hand, the calculations on CH_3^- by Driessler *et al.* [11] indicated that over an 18° interval of the out of plane angle there is a correlation energy variation of 0.5 kcal/mole that by *linear interpolation* would give an estimated 0.15 kcal/mole over a 6° interval. A similar change of E_{corr} in our case would effectively remove the entire barrier. However, there is no reason to assume that the $E_{corr}(\gamma)$ function is linear. Rather, one may expect very little change of E_{corr} in the immediate neighbourhood of the point $\gamma = 90°$, since there

$$\frac{\partial E_{corr}}{\partial \gamma} = 0$$

due to symmetry. This suggests that the variation of correlation energy does not exceed that of the total energy and the qualitative conclusion of the pyramidality of the carbanion $^\ominus:CH_2-CN$ appears to be significant, although an extremely flat minimum potential cannot be ruled out with certainty. Electron withdrawing groups in general tend to increase barrier heights while conjugating groups tend to diminish them. It appears that in the case of

$$\overset{\textstyle O}{\underset{\textstyle -C-H}{\|}} \quad \text{and} \quad -NO_2$$
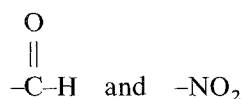
groups the conjugative effect wins over the electron withdrawing ability of this group, in the case of the $-C\equiv N$ group the electron withdrawing effect dominates, resulting in a slightly pyramidal structure.

3. Conclusions

It appears that in actual chemical systems the counter ion and solvent have a decisive role in determining the most favourable geometry of this unusual carbanion, and *both* pyramidal and planar $^\ominus:CH_2-CN$ ions do exist. The theoretically predicted easy deformability of the $^\ominus:CH_2:CN$ carbanion centre is supported by earlier experimental results on $M^{\oplus\ominus}:CH_2-CN$ systems [3, 4] and resolves a seemingly contradictory duality in the interpretation of those experimental findings.

The present calculations are also of some computational interest regarding the qualitative conclusions obtained with various basis sets. The result obtained with the 4-31G basis set, generally regarded much more reliable than any of the 3G and 4G minimum bases, appears to be out of line, not only with respect to the predicted planar structure, but also by indicating a potential curve that is qualitatively different in shape from the other three. If one disregards the fine variations on the bottom of the curves, all three of the 3G, 4G and Uniform Quality basis calculations show a wide, relatively flat region that is much less pronounced in the case of the 4-31G result. Consequently, the minimum basis calculations appear to be qualitatively more in agreement with the polarized basis result than the 4-31G calculations, contrary to expectation. It is conceivable that an even larger U.Q. basis and polarization function optimized directly for negative ions, as well as the

inclusion of correlation energy corrections would alter the results slightly, however, the qualitative conclusion on the extreme flatness of the potential is expected to be invariant under any further improvement of the wavefunction.

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