84. Nitrocyclopropyl-Anion: A Triplet Ground State Molecule?

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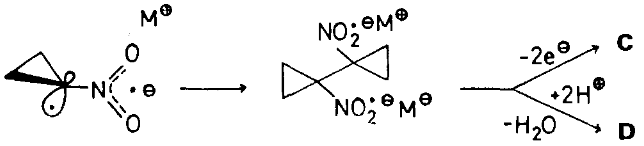
Summary

STO-3G calculations show that the nitrocyclopropyl anion prefers a triplet ground state with a tetrahedral C(*a*)-atom and a perpendicular orientation of the three-membered ring and the NO_2-group, **1**-90° *(Table 1)*. This unusual result is in agreement with recent experimental findings of *Kai et al.* (Helv. Chim. Acta *65*, 137 (1982)). Other NO_2-anions as well as all CHO-, COOH- and CN-substituted anions **2**–**12**, have singlet ground states **2**-0°-**12**-0° *(Table 1)*, in agreement with copious experimental data (*Wagner & Boche*, Z. Naturforsch. *37b*, 1339 (1982)).

During the preparation of a recently published paper [1], we noted that the nitrocyclopropyl anion **1** is the only one of eighteen carbanions which prefers a triplet ground state at the STO-3G level. Since this result was rather unusual, and since it was known that simple SCF-calculations overestimate the stability of triplet compared to singlet configurations [2], we held back these findings. Since then, however, *Kai et al.* [3] have invoked this triplet species **A**-90°-M to explain the elusive nature of the nitrocyclopropyl anion: deprotonation of nitrocyclopropane led under all conditions to 1,1′-dinitrobicyclopropyl (**C**) and 1-nitro-1′-nitrosobicyclopropyl (**D**), possibly *via* **A**-90°-M and its dimer **B**-2M [3].

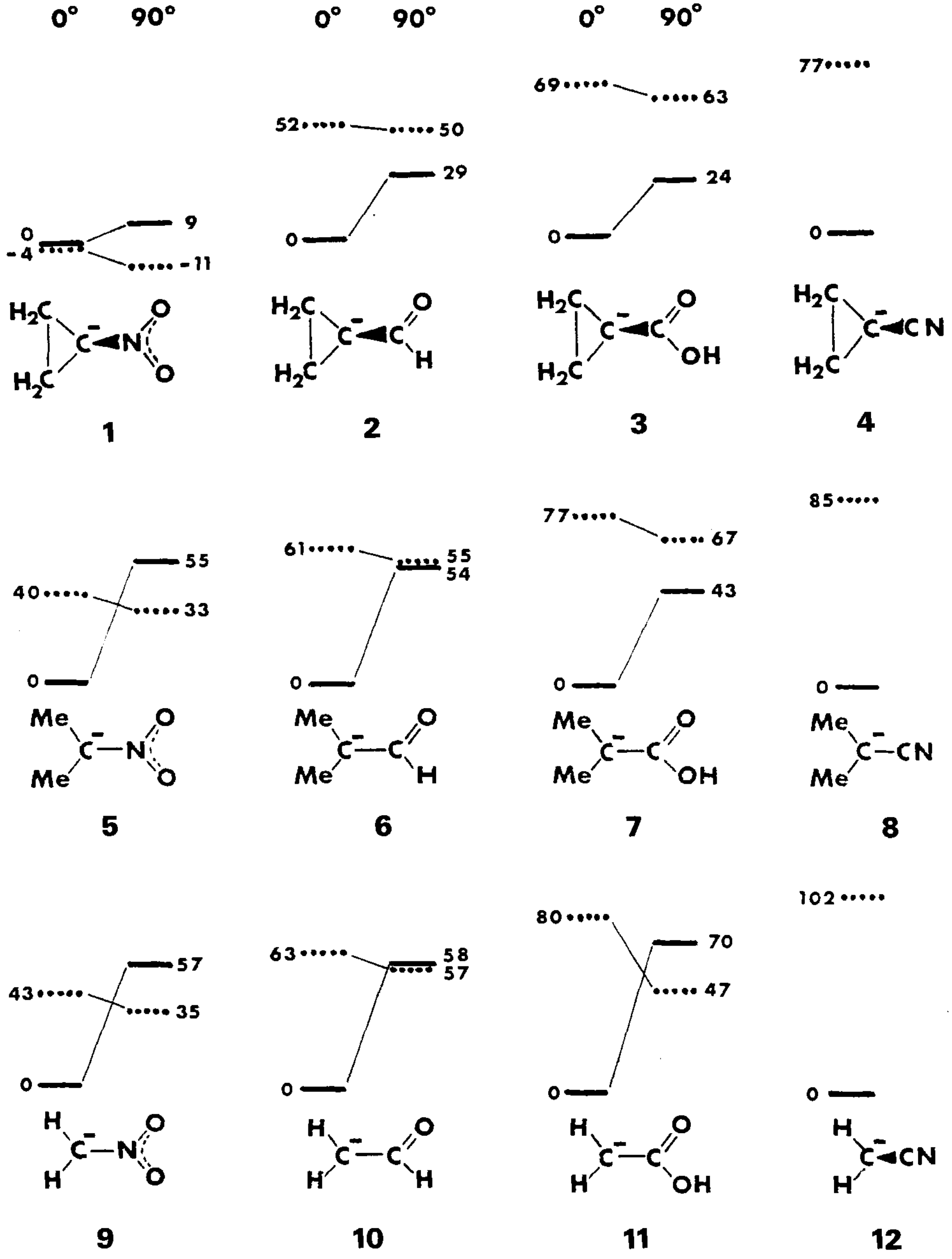


A-90°-M **B**-2M

The relative STO-3G energies [kcal/mol] of the singlet and triplet states of the twelve substituted carbanions **1**–**12** clearly reveal the peculiarity of the nitrocyclopropyl anion **1** *(Table 1)*.

One can see from *Table 1* that: *a)* the singlet/triplet energy gaps in the 0°-conformations are generally smaller in the case of the nitro anions **1**, **5** and **9**;

Table 1. *Relative STO-3G energies* [kcal/mol] *of the singlet* (▬) *and triplet* (•••) *states of the acceptor substituted carbanions* **1**–**12**. The energies are related to the STO-3G singlet energies (0–) of the STO-3G geometry optimized carbanions **1**–**12** (see also *Table 6* in [1]). Values for 90° correspond to the perpendicular orientation of the three-membered ring and the substituents NO_2, CHO and COOH. The singlet and triplet energies in a 0°- (and in a 90°-)conformation were calculated with the same geometries.



b) the nitro substituent is able to stabilize a neighboring carbanion center both by conjugative and inductive effects [1], in agreement with recent results of *Lipkowitz* found by ^{17}O-NMR. chemical shifts [4]; *c)* the cyclopropyl anions **1–4** prefer a tetrahedral to a trigonal conformation of the C(*a*)-atom, which favors the triplet state. This preference is not hindered by the nitro substituent.

The extraordinary stability of **1** in the triplet state is found only for the tetrahedral conformation of the C(*a*)-atom. If the conformation is held trigonal the triplet state becomes 43 kcal/mol less stable than the singlet and **1** shows the same behavior as the other anions **2–12**.

Finally, we would like to emphasize that these STO-3G calculations can only reveal a tendency, albeit a significant one. Elaborate calculations with basis sets augmented by diffuse orbitals [5] and including configuration interaction should give more reliable results.

REFERENCES

[1] *H.-U. Wagner & G. Boche*, Z. Naturforsch. *37b*, 1339 (1982), and ref. cited in this paper.

[2] a) *J.F. Harrison*, Acc. Chem. Res. *7*, 378 (1974); b) *C.F. Bender, H.F. Schaefer III, D.R. Franceschetti & N.C. Allen*, J. Am. Chem. Soc. *94*, 6888 (1972).

[3] *Y. Kai, P. Knochel, S. Kwiatkowski, J.D. Dunitz, J.F.M. Oth, D. Seebach & H.-O. Kalinowski*, Helv. Chim. Acta *65*, 137 (1982).

[4] *K.B. Lipkowitz*, J. Am. Chem. Soc. *104*, 2647 (1982).

[5] *J. Chandrasekhar, J.G. Andrade & P.v.R. Schleyer*, J. Am. Chem. Soc. *103*, 5609 (1981).