

Ab-initio Calculation on Methylnitrenium Ion (CH₃NH)⁺

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Ab initio calculation were carried out on the singlet and triplet states of the methylnitrenium ion. The triplet state is the ground state for all values of angle at nitrogen.

In a recent communication¹ Koser reported semiempirical calculations on methyl (I)- and dimethylnitrenium ions with the intention to rationalize the reactivity data of the piperidine nitrenium (II) ion². The main conclusion of the INDO cal-

ulation was that the singlet and triplet states cross at some angle Φ . In this note a non-empirical calculation is reported on (I). The basis set of Pople et al.³ STO-3G was used and the triplet state energy was determined with the unrestricted Hartree-Fock method⁴. The angle Φ was varied from 90° to 180° and at every step the geometry optimizations of the CN and NH bond lengths were done. The changes in bond lengths are 0.044 Å (CN) and 0.006 Å (NH) for the triplet state. The numbers for the singlet state are 0.04 Å and 0.031 Å. The minimum energy (Fig. 1) is at $\Phi \approx 110^\circ$ for the singlet state and at $\Phi \approx 150^\circ$ for the triplet state. There is no crossover and even the energy difference is quite large. The smallest difference is at 90° and amounts to 20 kcal/mol. A few point calculations on the dimethylnitrenium ion have shown that there is no crossover as in (I). If this type of calculation can be used to rationalize the exclusive triplet reactivity² of (II) than there is no need to involve a singlet-triplet conversion as supposed in Reference¹.

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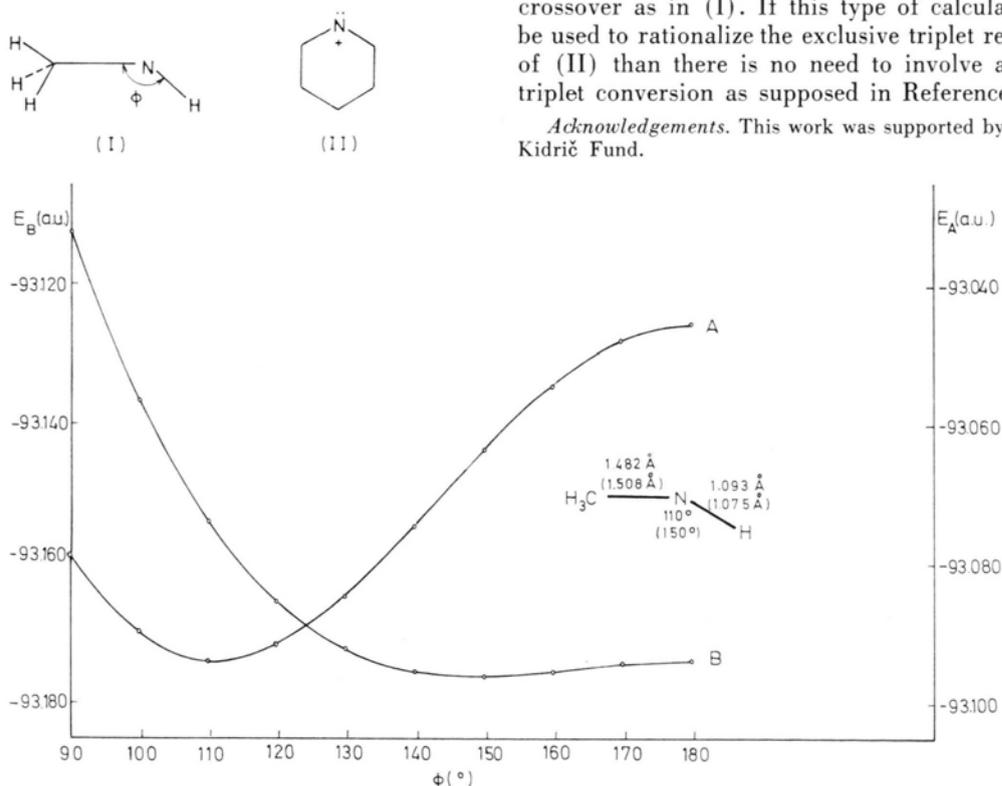


Fig. 1. Energies of the singlet (A) and triplet (B) state (in a.u.). Geometry at minimum energy for the singlet (triplet) state.

¹ G. F. Koser, J. Chem. Soc. Chem. Commun. **1973**, 461.

² P. G. Gassman and C. D. Hartman, J. Amer. Chem. Soc. **95**, 449 [1973].

³ W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 [1969].

⁴ J. A. Pople and R. K. Nesbet, J. Chem. Phys. **22**, 571 [1954].