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Semiempirical Molecular Orbital Calculations on Unconstrained Alkylnitrenium Ions

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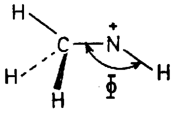
Summary SCF–MO calculations of the INDO type were carried out on the low-lying singlet and triplet states of methylnitrenium ion and staggered dimethylnitrenium ion; energies were determined as a function of geometry at nitrogen.

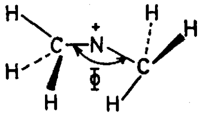
We report the results of INDO calculations[1] on the low-lying singlet and triplet electronic states of methylnitrenium ion (I) and dimethylnitrenium ion (II) and comment on the chemical implications of these calculations.

Although the chemistry of (I) and (II) has not yet been elucidated, Gassman and his co-workers have reported experimental evidence for the transient existence of nitrenium ions when *N*-chloramines [2,3a,3b] and cyclic *N*-hydroxylamine benzoates[4] are solvolysed in methanol. They have discerned a chemical distinction between the singlet and triplet electronic modifications of these species.[2] Whereas (III) exhibits typical onium ion reactivity and leads to products of skeletal rearrangement and solvent incorporation at carbon, (IV) behaves as a free radical and, in the presence of methanol, affords the ammonium ions (V), presumably *via* hydrogen atom abstraction from carbinol carbon.[2] Spin inversion in (III) can, in some instances, be catalysed by heavy-atom solvents since the presence of such solvents leads to increased yields of (V) relative to singlet products.[2]

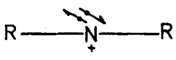
In view of the formal resemblance of nitrenium ions and carbenes, we were perplexed by the recent report that the piperidine nitrenium ion (VI), when generated in methanol in the absence of heavy-atom solvents, leads exclusively to the triplet product (VII).[4] Carbenes readily insert into oxygen-hydrogen bonds,[5a] and, to our knowledge, reduction of carbenic carbon in alcohols has not been observed. Moreover, the singlet carbene (VIII), the electronic analogue of (VI), isomerizes rapidly and efficiently to cyclohexene.[5b] It is known that the relative energies of singlet and triplet carbenes are a function of geometry at carbenic carbon, and it seemed likely that the internal carbon–nitrogen–carbon bond angle in (VI), being constrained to *ca.* 109°, might 'force' the singlet and triplet states of (VI) to be nearly isoenergetic. In that event, spin inversion in (VI) could



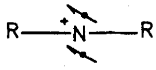
(I)



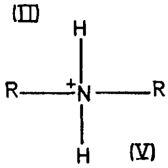
(II)



(III)

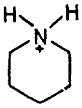


(IV)

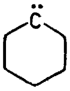


(V)

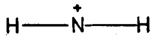
(VI)



(VII)



(VIII)



(IX)

take place so readily that competitive singlet chemical reactivity would be eliminated.

Following the success of semiempirical MO procedures in predicting the properties of carbenes,[6a–c] we studied the exclusive triplet reactivity of (VI), a dialkylnitrenium ion, by conducting SCF–MO calculations of the INDO type. Energy calculations on simple, unconstrained alkylnitrenium ions have not been reported and therefore we choose (I) and (II) in the indicated conformations as model compounds. As ϕ was varied in 10° increments from 90 to 180°, the potential energy curves in Figures 1 and 2 were generated, the (X,Y,Z) co-ordinates of each atom for each value of ϕ being determined by use of the model builder program developed by Gorden and Pople.

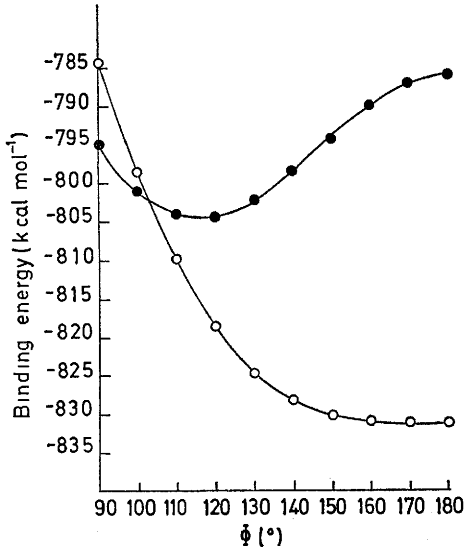


FIGURE 1. *Binding energies of the singlet (●) and triplet (○) electronic states of methylnitrenium ion as a function of ϕ.*

The triplet states of the nitrenium ions (I) and (II), at their minimum energy configurations, are predicted to be more stable than the corresponding singlet states at their minimum energy configurations by 27 and 26 kcal mol^{-1}, respectively. The potential minima for singlet dimethylnitrenium ion (at $\phi = 122°$) and singlet methylnitrenium ion (at $\phi = 118°$) indicate that the former species should be slightly more linear than the latter, possibly owing to steric effects. The triplet electronic states for the nitrenium ions (I) and (II) should assume nearly linear geometries. As ϕ is diminished systematically from 180°, the singlet–triplet energies of (I) and (II) converge and finally cross at 103° for (I) and 112° for (II). Thus, if ϕ were constrained to 90°, the singlet states of (I) and (II) would be expected to be the ground states (by 10 and 37 kcal mol^{-1}, respectively).

Two *ab initio* treatments of the parent nitrenium ion (IX) have appeared,[7] and, although similar energy convergence is predicted for the low-lying singlet and triplet electronic states no crossover is observed as ϕ is varied between 90 and 180°.

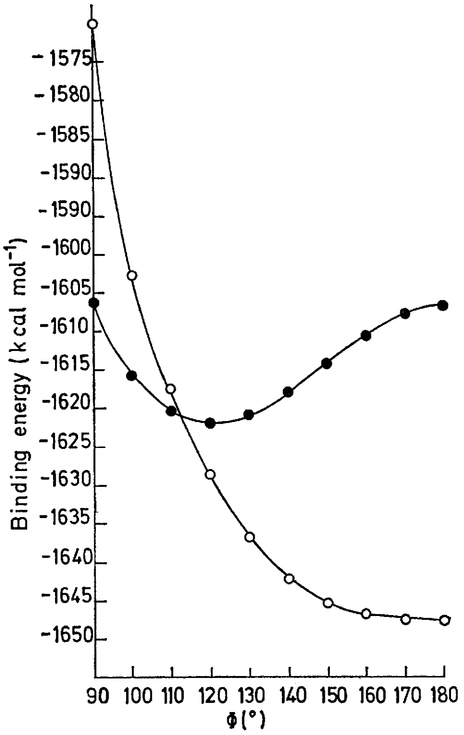


FIGURE 2. *Binding energies of the singlet (●) and triplet (○) electronic states of staggered dimethylnitrenium ion as a function of ϕ.*

The results of our calculations are consistent with chemical experience. Figure 2 shows that at ϕ values near 109°, the singlet–triplet energies of dialkylnitrenium ions are very close [*ca.* 3 kcal mol^{-1} for (II)], and singlet–triplet interconversion should, therefore, occur readily. On this basis, the exclusive triplet reactivity of (VI) can be rationalized.

Finally, if the C–N–C angles of dialkylnitrenium ions were constrained to either 180° or 90°, spin inversion should be less efficient and singlet chemical reactivity might be expected.

Although INDO calculations cannot predict energy separations with the same accuracy as some other methods, the relative energy trends predicted here appear to be reliable.

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