# On the Possibility of Isolating Diazirine *N*-Oxides



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*Ab initio* molecular orbital calculations at the 6-31G* level predict that diazirine *N*-oxide is more stable with respect to its constituent fragments, singlet $CH_2$ and $N_2O$, than diazirine is with respect to singlet $CH_2$ and $N_2$. In view of these results and the many diazirines which have been reported, it is suggested that it may be possible to detect a suitably substituted diazirine *N*-oxide.

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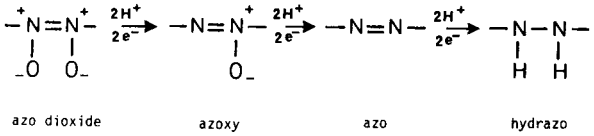
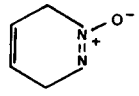
In a formal sense the azo functional group is related to the hydrazo, azo *N*-oxide (or azoxy) and azo dioxide groups by the following two-electron reduction sequence:




Numerous examples in which these dinitrogen functional groups are incorporated into six-membered rings are known (1). To a lesser extent examples of larger and smaller rings have been isolated. In the case of three-membered rings, the parent azo compound, diazirine and many of its alkyl, phenyl, halo, *etc.*, derivatives have been prepared (2), but no diazirine *N*-oxides have been reported. This is noteworthy in view of the chemistry of the larger ring systems, of which, the azocyclohexene **1** and the corresponding *N*-oxide **2** are prototypes.

1



2

Deazetation of **1** is thought to occur in a single step whereby both C-N bonds cleave simultaneously in concert with bond formation in the product fragments (3). Furthermore derivatives of **1** are difficult to detect whereas the *N*-oxides can be isolated under ambient conditions as crystalline solids (4). At elevated temperatures, derivatives of **2** lose $N_2O$ (5, 6).

The absence of diazirine *N*-oxides in the chemical literature, despite the greater stability of cyclic azoxy compounds relative to the corresponding azo compounds (7), has prompted us to use *ab initio* molecular orbital (MO) calculations to consider the thermodynamic stability of diazirine *N*-oxide with respect to its constituent fragments, singlet $CH_2$ and $N_2O$. To this end *ab initio* calculations were carried out by use of the PHANTOM program (8). Following Snyder and Basch (9), a double-zeta (DZ) basis set of Gaussian-type orbitals formed from the contracted s-type functions of Whitten (10) and the p-type functions of Huzinaga (11) was selected. Additional calculations were carried out at the STO-3G (12) and 6-31G* (13) levels by use of the GAUSSIAN 76 program (14). For each species studied in this communication, the energy was minimized with respect to all structural parameters subject to the point group of the most stable molecular conformation.

Tables 1 and 2 summarize the principle results for diazirine and diazirine *N*-oxide, respectively. At the DZ level, diazirine *N*-oxide is predicted to be ~ 23 kcal/mole more stable than the fragments, singlet $CH_2$ and $N_2O$, while the deazetation of diazirine is predicted to be only slightly endothermic. As a check on the importance of including polarization functions in the basis set we have carried out 6-31G* calculations on the STO-3G equilibrium geometries of diazirine and its *N*-oxide, and we have obtained ~6 and 19 kcal/mole for the respective dissociation energies. Due to limitations on computer time we have not optimized the structures of the cyclic compounds at the 6-31G* level. On the basis of previous experience, we expect that geometry optimization would increase the dissociation energies of diazirine and its *N*-oxide by ~2-3

Table 1

Computed Properties of Diazirine

| | Basis set | | |
|---|---|---|---|
| | STO-3G | DZ | 6-31G* |
| Total energy (au) | −145.94650 | −147.72887 | −147.82567 (a) |
| Dissociation energy (kcal/mole) | 46.2 | 0.1 | 5.9 (b) |
| Equilibrium geometry (c) | | | |
| r(NN) | 1.266 | 1.226 | |
| r(CN) | 1.488 | 1.500 | |
| r(CH) | 1.086 | 1.071 | |
| ∠ (HCH) | 117.0 | 119.0 | |

(a) Computed at the STO-3G equilibrium geometry. (b) Based on the 6-31G*//STO-3G energy of diazirine and the 6-31G*//6-31G* energies (18) of $CH_2$ and $N_2$. (c) the corresponding experimental values (19) are 1.228, 1.482, 1.090 Å, and 117.0°, respectively.

Table 2

Computed Properties of Diazirine *N*-Oxide

| | Basis set | | |
|---|---|---|---|
| | STO-3G | DZ | 6-31G* |
| Total energy (au) | −219.68291 | −222.47602 | −222.58238 (a) |
| Dissociation energy (kcal/mole) | 66.4 | 22.6 | 18.8 (b) |
| Equilibrium geometry | | | |
| r(NN) | 1.315 | 1.25 | |
| $r(N_1O)$ | 1.268 | 1.26 | |
| $r(CN_1)$ | 1.459 | 1.44 | |
| $r(CN_2)$ | 1.520 | 1.49 | |
| r(CH) | 1.090 | 1.08 | |
| ∠(NNO) | 145.9 | 152. | |
| ∠(HCH) | 116.0 | 117. | |

(a) Computed at the STO-3G equilibrium geometry. (b) Based on the 6-31G*//STO-3G energy of diazirine *N*-oxide and the 6-31G*//6-31G* energies (18) of $CH_2$ and $N_2O$.

and 3-5 kcal/mole, respectively. The much larger dissociation energies obtained with the STO-3G basis set are consistent with the tendency of this minimal basis set to favour cyclic molecules (15, 16).

In view of earlier studies of the structures and stabilities of three-membered rings (15) with the STO-3G, 4-31G, and 6-31G* basis sets, we believe that the 6-31G* results reported here provide a semi-quantitative estimate of the dissociation energies described above. At the 6-31G* level, diazirine *N*-oxide is predicted to be stable with respect to the loss of $N_2O$ by about 13 kcal/mole more than the heat of reaction for the deazetation of diazirine. Since many diazirines (2, 17) are known, we consider the detection of a suitably substituted diazirine *N*-oxide to be very probable.

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