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MNDO Calculations on Diazirines

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The MNDO molecular orbital method gives good agreement between experimental geometries and, when available, heats of formation of diazirines. MNDO and *ab initio* calculations have been performed on a novel intermediate, methylenediazirine, proposed in a reaction of 3-chloro-3-methyldiazirine. The relation of this intermediate to its diazo-isomer, its dimer and the products of the reaction are discussed on the basis of MNDO calculations.

Key words: MNDO – Diazirines – Methylenediazirine ~ Reaction of

1. Introduction

Diazirines are interesting compounds because of the presence of the azo linkage in a three-membered ring. The ring is surprisingly unreactive toward a variety of reagents [1–3]. Diazirines lose nitrogen by unimolecular reaction thermally or photochemically and can also form the diazo-isomers [4–15]. There is considerable experimental data on the geometries of diazirines [16–20]. The heat of formation of the parent compound is a subject of controversy [21]. Two independent determinations of the heat of formation of 3-chloro-3-methyldiazirine have been made [22, 23].

A MINDO/2 study of the equilibrium geometries of several diazirines, their diazo-isomers and derived carbenes has been done [24]. MINDO/3 seriously

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underestimates the heat of formation of 3H-diazirine, the parent compound [25]. *Ab initio* calculations on the parent compound have been performed [21, 26–29] but it is not easy to judge the reliability of these results because of the uncertainty in the heat of formation of this compound.

Compared to the INDO level, the NDDO level of approximate molecular orbital theory should be considerably better for compounds with significant lone pair interactions such as diazirines. The MNDO method of Dewar's group would seem to be an ideal semi-empirical method for studying these compounds [30–32]. We have undertaken a systematic study of several known diazirines using MNDO [33] and have also studied the properties of methylenediazirine with MNDO.

2. Ground States of Diazirines

In Table 1 the experimental properties of diazirines are compared with the values calculated using MNDO. The geometrical parameters are defined in Fig. 1.

The agreement between observed and calculated properties is generally excellent. It is especially gratifying to find good agreement for 3-chloro-3-methyldiazirine because the nitrogen-chlorine interactions have not been explicitly parameterized in MNDO. The transferability of one-centre parameters [30] works very well in this case, a clear advantage over MINDO/3. In view of the good agreement with the heat of formation of 3-chloro-3-methyldiazirine, the calculated value of 303.5 kJ mol^{-1} for 3H-diazirine gives support to the experimentally estimated value of 332 kJ mol^{-1} [21].

3. Methylenediazirine

Methylenediazirine has recently been proposed as an intermediate in the reaction of 3-chloro-3-methyldiazirine with hydrogen atoms (*vide infra*) [34]. The properties of this unknown diazirine calculated by MNDO are displayed in Fig. 2.

Ab initio calculations on methylenediazirine were performed with STO-3G [35] and 6-31G [36] basis sets. The geometry was first optimized with the STO-3G basis set [37]. The results agree well with the MNDO geometry except for the nitrogen–nitrogen bond length which is predicted to be longer according to STO-3G (Fig. 2). For 3H-diazirine itself the nitrogen–nitrogen bond length is predicted to be too long by STO-3G compared to 6-31G [21] and experiment [16]. Indeed, the energy of methylenediazirine calculated with the 6-31G basis set and MNDO geometry, −185.522 hartree, is lower than the energy calculated with the 6-31G basis set and STO-3G geometry, −185.518 hartree. The MNDO geometry is obviously the better one.

A significant difference between the MNDO and *ab initio* calculations is that MNDO predicts the negative end of the carbon–carbon bond dipole to be the ring carbon while the *ab initio* calculations predict the reverse, the trend increasing from STO-3G to 6-31G. It has previously been suggested on the basis of INDO calculations that the diazirinyl cation has aromatic character [38] and the *ab initio*

Table 1. Observed and calculated properties of diazirines

X	Y	r_1	r_2	r_3	r_4	Θ_1	Θ_2	Θ_3	Θ_4	μ	ΔH_f^o	Refs.
H	H	122.9	148.8	109.8	109.8				114	1.55	303.5	16, 21
		122.8	148.2	109	109				117	1.59	255–435	
F	F	124.1	148.6	132.4	132.4	49.36			112.7	0.57	−88.9	
		129.3	142.6	131.5	131.5	53.95			111.84			17
H	CH_3	122.8	149.3	110.4	151.0			125.6		1.60	260.8	
		123.5	148.1		150.1			122.3		2.03		18
CH_3	CH_3	122.6	150.0	152.1	152.1				116.8	1.61	230.0	
		123.5	149.0	149.9	149.9				119.7	2.19		19
CH_3	Cl	123.1	148.7	151.2	177.1	48.9	127.2	118.3		1.69	233.2	
		124.1		149.8	174.3	50.2	116.7	116.7			239.0	20, 22, 23

Geometries as in Fig. 1, bond lengths, r, in *pm*, bond angles Θ, in degrees. Dipole moments, μ, in debyes. Heats of formation, ΔH_f^o, in kJ mol^{-1}. For each compound calculated values are given in the top line and observed in the bottom line.

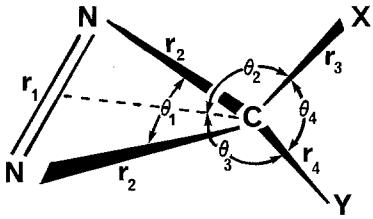


Fig. 1. Experimentally determined bond lengths, r, and bond angles, Θ, of diazirines

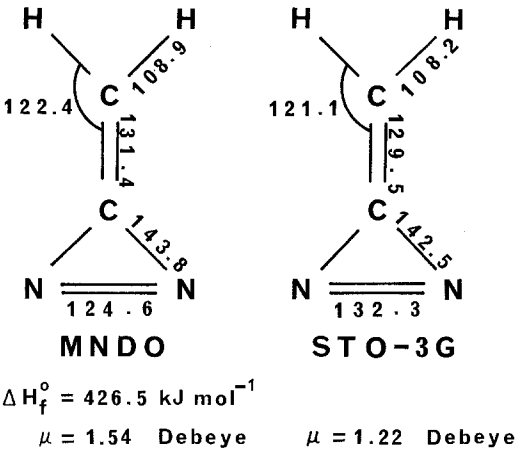


Fig. 2. Calculated properties of methylenediazirine. Bond lengths in pm, bond angle in degrees

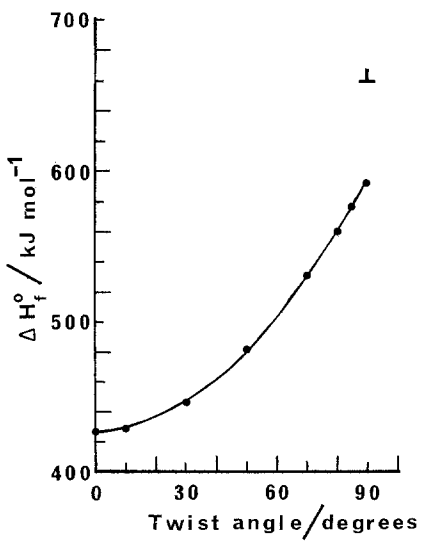


Fig. 3. Rotational barrier for twisting one hydrogen of methylenediazirine. The perpendicular form (see text) is indicated by ⊥

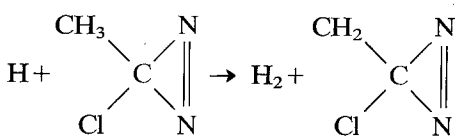
charge distribution of methylenediazirine could imply that the ring derives some stability by electron withdrawal.

The importance of conjugation with the exocyclic methylene carbon was investigated first with MNDO by twisting one hydrogen out of the plane and optimizing

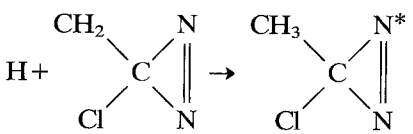
all other geometrical parameters. The results, plotted in Fig. 3, show a substantial rotational barrier. The ring carbon and exocyclic methylene are not co-planar according to MNDO, except for the most stable conformation in which all atoms are co-planar. Qualitative inspection of the MNDO molecular orbitals shows this is because the highest occupied molecular orbital is more stable if it maintains some π-bonding. In the perpendicular form this orbital loses its π character and the energy of the molecule increases by 70 kJ mol^{-1} ($\perp$ in Fig. 3).
For the 90° twist angle these calculations were repeated with the 6-31G basis set and, in view of the discussion above, MNDO optimized geometries. The *ab initio* calculation predicts the perpendicular form to be 130 kJ mol^{-1} less stable. Overall, it may be concluded from both MNDO and the *ab initio* calculations that conjugation of the ring with the methylene carbon is important. The MNDO rotational barrier is 166 kJ and the *ab initio* rotational barrier (6-31G with MNDO geometries) is 223 kJ.

4. Reactions of Methylenediazirine

The reaction of 3-chloro-3-methyldiazirine with hydrogen atoms gives acetonitrile as a major product [34]. Studies with deuterium atoms and the deuterated diazirine suggest the following pathways to account for experimental results.



(4.1)



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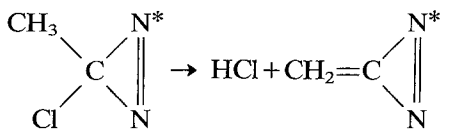
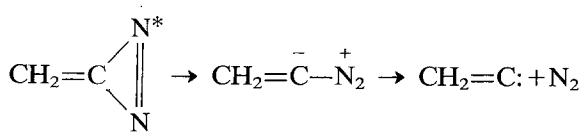
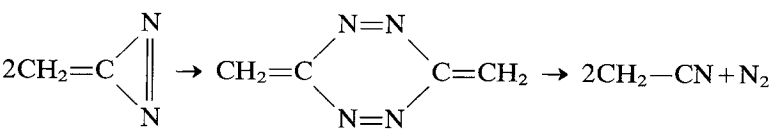


(4.3)



(4.4)



(4.5)

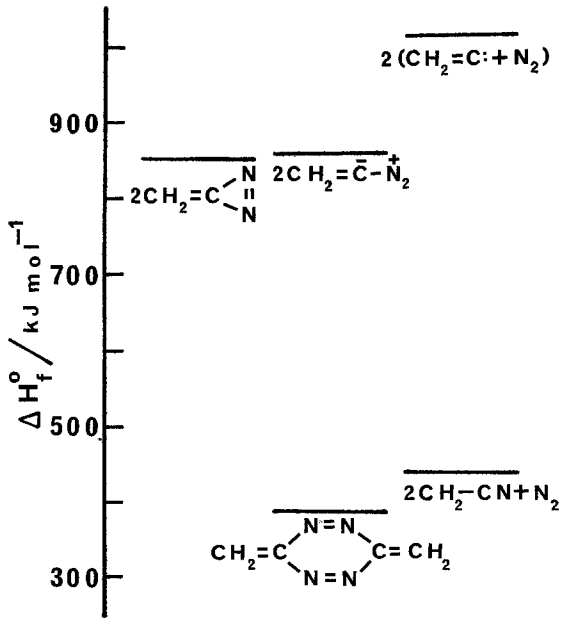


Fig. 4. Cuts from the potential surface of methylenedizairine

The first steps, (4.1–2), are analogous to those used to explain the activation of alkyl halides [39]. Methylenediazirine is the key intermediate in this mechanism. The isomerization to diazoethene, (4.4), is reasonable [13–15], but diazoethenes do not appear to give nitriles as products [40]. The last step, (4.5), produces acetonitrile radicals after dimerization to a tetrazine. Heats of formation of these intermediates calculated with MNDO are shown in Fig. 4.

If methylenediazirine is sufficiently energized these pathways should be feasible. The energy would have to come from the step in which HCl is eliminated from activated 3-chloro-3-methyldiazirine, (4.3). There is some experimental evidence that much of the available energy from such eliminations is carried by the polyatomic fragment [41, 42].

5. Conclusions

MNDO gives excellent results for diazirines and is a great improvement over MINDO/3 for these compounds. In view of this good agreement some confidence may be attached to the MNDO predictions for methylenediazirine and its reactions. With this as a guide experimental studies on the reaction in which methylenediazirine was proposed as an intermediate are in progress.

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