

this case would represent the largest value for  $K$ . In this case the distance would be  $2^{1/2}r$ . Thus interelectron distance would vary between  $2^{1/2}r$  and  $2r$ . If repulsion within an orbital is inversely proportional to  $r$ , i.e.,  $A_A \propto 1/r$ , then approximate limits for  $K$  are  $0.71 \geq K \geq 0.5$  (i.e.,  $1/2^{1/2} \geq K \geq 1/2$ ).

The value  $K = 0.67$  falls within these bounds and when substituted into the repulsion term gives  $A_A(1 - 0.33\delta_{A_j})$ . This yields

eq 2 when combined with (14) and the relations of paper 1. The good correlation with other schemes and the simplicity of (2) suggest that the value is reasonable. Further correlations will be necessary to verify this estimate.

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## SINDO1 Study of Photochemical Reaction Mechanisms of Diazirines

Peter L. Müller-Remmers and Karl Jug\*

Contribution from Theoretische Chemie, Universität Hannover, 3000 Hannover 1, Federal Republic of Germany. Received June 1, 1984

**Abstract:** The photochemical reaction mechanisms of diazine, 3,3-dimethyldiazirine, and 3-formyldiazirine were studied with the semiempirical MO method SINDO1. The properties of equilibria and transition states as well as diradical and zwitterionic intermediates were calculated on configuration interaction (CI) potential surfaces. It is shown that the substituents have a decisive influence on the relative energy of the singlet and triplet surfaces to the ground state. Therefore, localized excitations can initiate reactions which lead primarily either to carbenes or to diazomethanes. A classification of the photochemical reaction mechanisms of diazirines is discussed. Good agreement is obtained with available experimental results.

### 1. Introduction

The discovery of the diazirines<sup>1,2</sup> in 1960/61 concluded the discussion about the open or cyclic structure of diazo compounds.<sup>3</sup> The interest in the research in this field of heterocycles is undiminished even today.<sup>4,5</sup> There are still controversies about the photolytic and thermolytic reaction mechanisms of diazirines.<sup>4,6,7</sup> It is known that the cyclic compounds are experimentally more easily accessible and thermodynamically more stable than their linear isomers.

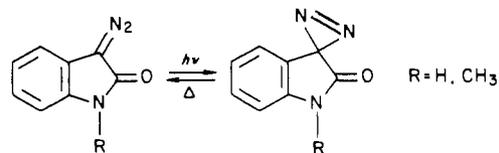
The difficulties with the interpretation of reaction pathways may be discussed in a few examples. Amrich and Bell<sup>8</sup> obtained 20% diazomethane in the photolysis of diazirine in the gas phase. In the photolysis of diazirine in a <sup>15</sup>N<sub>2</sub> matrix, Moore and Pimentel<sup>9</sup> found diazomethane, which originates from the reaction of methylene with the <sup>15</sup>N<sub>2</sub> matrix, as secondary product. Frey<sup>10</sup> concludes that the diazomethane generated in the gas phase must appear through intersystem crossing (ISC) in its first triplet state.

3-Chloro-3-methoxydiazirine<sup>11</sup> and 3,3-dimethyldiazirine<sup>12</sup> decompose thermally in first-order reactions into nitrogen and the corresponding carbenes and their conversion products. It is not clear whether the ring bonds are cleaved in a synchronous or sequential homolytic or heterolytic fashion and whether transition states or intermediates have diradical or zwitterionic character.

High preexponential factors would suggest acyclic diradical transition states. It is an open question why linear diazo compounds are not found as products.

Schmitz<sup>3</sup> states that the diazirine is destabilized by an  $\alpha$ -keto group compared to the alkyl-substituted compound. Thus  $\alpha$ -ketopentamethylenediazirine loses nitrogen already at 40 °C whereas pentamethylenediazirine requires 160 °C for the analogous reaction. Liu<sup>4</sup> postulates very generally ionic transition states for the decomposition of diazirines.

An interesting, but mechanistically not clarified topic is the chemistry of  $\alpha$ -diazamides. They are representatives of those linear diazo compounds which are known to lead photolytically to a moderate yield of ring closure. Voigt and Meier<sup>13</sup> report in this context an interesting equilibrium in the photochromic system

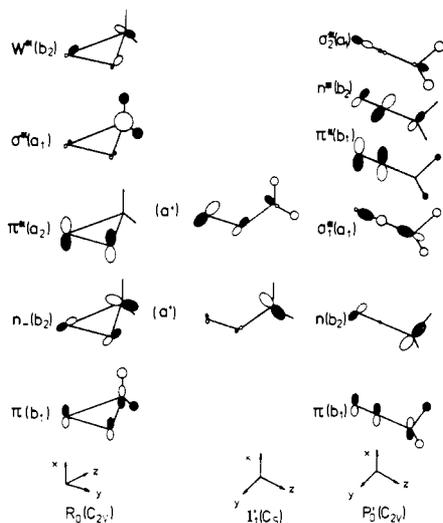


3-diazo-2-oxoindoline/2-oxospiro[diazirine-3,3'-indoline]. The linear diazo compound can be converted to the cyclic form by irradiation, and the latter thermally reverts to the former after a short time.

Theoretical investigations of diazirines are scarce. Among them are studies on the vertical excitation energies of diazirine, diazomethane,<sup>14-18</sup> and 3,3-difluorodiazirine.<sup>15,16</sup> Hoffmann<sup>18</sup> examined the photochemical behavior of diazirine with the extended Hückel method. Later Devaquet<sup>17</sup> studied the same molecule by

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**Figure 1.** Photochemically relevant MO's of diazirine, diazomethane, and intermediate  $I_1'$ .

an ab initio procedure. No geometry optimization was attempted. To our knowledge no further theoretical studies on substituted diazirines and diazomethanes have been made.

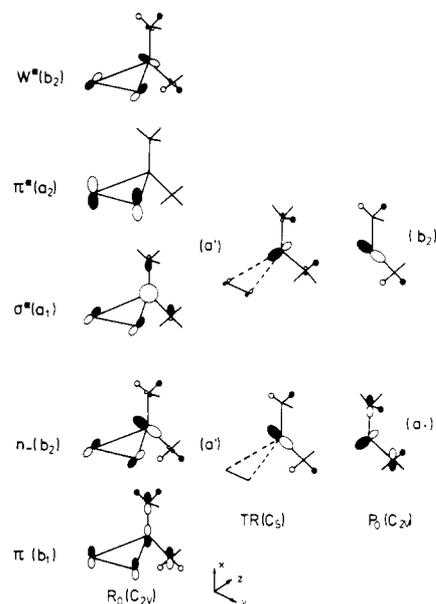
In the present work, the energy hypersurfaces of excited states of diazirine, 3,3-dimethyldiazirine, and 3-formyldiazirine are investigated to obtain information about the photochemical reaction behavior of these molecules. For comparison, the thermal mechanisms on the ground-state surface are considered.

## 2. Description of the Method of Calculation

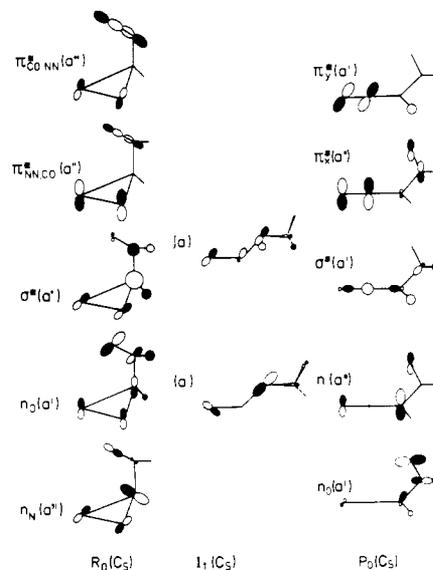
For the calculations the semiempirical molecular orbital (MO) method SINDO1<sup>19</sup> is used together with configuration interaction (CI). SINDO1 has been tested for a representative number of molecules with first-row atoms and found superior to MINDO/3 and MNDO.<sup>20</sup> The average errors of binding energies are 8–9 kcal/mol, of bond lengths 0.028 Å, and of bond angles 2.5°. Starting from the equilibrium geometry of the diazirines and diazomethanes in the ground state, we consider first all vertical single excitations from the two highest occupied to the three lowest unoccupied MO's and the double excitation from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO) plus further excitations into higher virtual orbitals if necessary. The calculation of extrema on the potential energy surface (PES) was performed with the Newton–Raphson method. Details of the procedure are published elsewhere.<sup>21,22</sup> For the excited triplet and singlet states which result from the above vertical excitations, the minima in the Franck-Condon region were calculated with optimization of all internal coordinates. A reaction pathway on an excited surface was investigated in such a way that the energy of the selected state was minimized along a representative coordinate, which shows a significant geometry change between reactant and product, with respect to all other internal coordinates. Parallel to this selected state, the vertical energies of the next higher and all lower states of the same spin multiplicity were calculated. The corresponding states of complementary spin, i.e., singlet for triplet and vice versa, were also calculated. All equilibria and transition states considered in the following were fully optimized.

## 3. Spectral Transitions

To analyze the optical spectrum of a chromophore, it is necessary to know the topology of the MO's responsible for the spectral transitions. We want to describe these MO's now briefly. In Figures 1–3 the highest occupied and lowest unoccupied orbitals



**Figure 2.** Photochemically relevant MO's of 3,3-dimethyldiazirine, dimethylcarbene, and transition region TR.



**Figure 3.** Photochemically relevant MO's of 3-formyldiazirine, 2-diazoacetaldehyde, and intermediate  $I_1$ .

of the molecules considered in this work are presented. We find only a shallow minimum for ground-state 2-diazoacetaldehyde and do not present it here. We will discuss this point further below.

**3.1. Description of the Molecular Orbitals.** The HOMO of diazirine (DI) and 3,3-dimethyldiazirine (DDI) is nonbonding and is denoted by  $n_-$ .<sup>17</sup> In 3-formyldiazirine (FDI) the HOMO is concentrated at the oxygen atom. We denote it by  $n_O$ . Here the next lower one is a  $n_N(n_-)$ . In all three cases, the next lower one than  $n_-$  is a  $\pi$  MO in the NN bond with some  $\pi_{CO}$  character in FDI. It should be mentioned at this point that the  $n_-$  and  $\pi$  MO's in DDI are destabilized compared to DI by nonbonding contributions from the methyl substituents. In FDI the CO substituent lowers the  $\pi$  MO and raises the  $n_N$  MO. The LUMO is a  $\pi^*$  in DI. The next higher one is a  $\sigma^*$  localized primarily at the ring carbon. The third virtual MO is of Walsh type ( $W^*$ ). In DDI,  $\sigma^*$  and  $\pi^*$  are exchanged because the methyl groups stabilize the  $\sigma^*$ . In FDI the substituent changes the topology of the  $\pi$  MO's. They contain contributions from the NN and CO bond. The LUMO is  $\sigma^*$  in the CC bond. Then a  $\pi^*_{NN,CO}$  follows with a major atomic orbital (AO) coefficient at both N atoms and small coefficients at C and O. Finally there is a  $\pi^*_{CO,NN}$  for which the weighting of the AO coefficients is reversed. In diazomethane

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Table I. Calculated Relative Energies (eV) of Excited States of Diazirine, Diazomethane, and Methylene<sup>j</sup>

	diazirine						diazomethane				methylene vertical	
	vertical		FC minima		intermediates		vertical		minima			
R <sub>0</sub>	<sup>1</sup> A <sub>1</sub>	0.0					P <sub>0</sub> '	<sup>1</sup> A <sub>1</sub>	0.0		<sup>3</sup> P <sub>0</sub>	0.0
<sup>3</sup> R <sub>1</sub> ( <sup>3</sup> n <sub>z</sub> π*)	<sup>3</sup> B <sub>2</sub>	4.25 (3.19, <sup>g</sup> 3.54 <sup>h</sup> )	<sup>3</sup> R <sub>1</sub>	4.12	I <sub>1</sub>	4.51	<sup>3</sup> P <sub>1</sub> ' ( <sup>3</sup> nσ*)	<sup>3</sup> B <sub>1</sub>	1.74		<sup>1</sup> P <sub>0</sub>	1.19
R <sub>1</sub> ( <sup>1</sup> n <sub>z</sub> π*)	<sup>1</sup> B <sub>2</sub>	4.59 (3.84, <sup>a</sup> 4.17 <sup>g</sup> )	R <sub>1</sub>	4.45	I <sub>1</sub> '	4.25	<sup>3</sup> P <sub>2</sub> ' ( <sup>3</sup> nπ*)	<sup>3</sup> A <sub>1</sub>	2.45		<sup>1</sup> P <sub>1</sub>	2.40
<sup>3</sup> R <sub>2</sub> ( <sup>3</sup> ππ*)	<sup>3</sup> B <sub>1</sub>	5.20 (5.03, <sup>g</sup> 5.10 <sup>h</sup> )	<sup>3</sup> R <sub>2</sub>	1.64	TR'	4.31	P <sub>1</sub> ' ( <sup>1</sup> nσ*)	<sup>1</sup> B <sub>1</sub>	2.81 (2.74 <sup>c</sup> )	2.66		
<sup>3</sup> R <sub>3</sub> ( <sup>3</sup> n <sub>z</sub> σ*)	<sup>3</sup> B <sub>1</sub>	5.35			TR	4.60	<sup>3</sup> P <sub>3</sub> ' ( <sup>3</sup> nπ*)	<sup>3</sup> A <sub>2</sub>	3.29 (2.84, <sup>i</sup> 2.72 <sup>h</sup> )			$E^3P_0 + E_{N_2} - E_{R_0} = 2.46$
<sup>3</sup> R <sub>4</sub> ( <sup>3</sup> n <sub>z</sub> W*)	<sup>3</sup> A <sub>1</sub>	5.56			<sup>3</sup> I <sub>1</sub> '	2.26	P <sub>2</sub> ' ( <sup>1</sup> nπ*)	<sup>1</sup> A <sub>2</sub>	3.49 (3.14, <sup>d</sup> 3.23 <sup>i</sup> )	3.13		
R <sub>2</sub> ( <sup>1</sup> n <sub>z</sub> σ*)	<sup>1</sup> B <sub>1</sub>	6.75 (6.2, <sup>b</sup> 7.7 <sup>h</sup> )					<sup>3</sup> P <sub>4</sub> ' ( <sup>3</sup> nσ*)	<sup>3</sup> B <sub>1</sub>	4.93			
							P <sub>3</sub> ' ( <sup>1</sup> nπ*)	<sup>1</sup> A <sub>1</sub>	5.75 (5.70, <sup>e</sup> 5.90 <sup>i</sup> )			
							P <sub>4</sub> ' ( <sup>1</sup> nσ*)	<sup>1</sup> B <sub>1</sub>	5.91			
$E_{P_0'} - E_{R_0} = 1.84 (1.30^f)$												

<sup>a-f</sup> Exptl: <sup>a</sup> Reference 23. <sup>b</sup> Reference 18. <sup>c</sup> Reference 28. <sup>d</sup> Reference 27. <sup>e</sup> Reference 29. <sup>f</sup> Reference 26. <sup>g-h</sup> Calcd: <sup>g</sup> Reference 15. <sup>h</sup> Reference 16. <sup>i</sup> Reference 14. <sup>j</sup> The energies are relative to the corresponding ground state R<sub>0</sub>, P<sub>0</sub>', <sup>3</sup>P<sub>0</sub> with experimental and other calculated values in parentheses.

Table II. Calculated Relative Energies (eV) of Excited States of 3,3-Dimethyldiazirine and Dimethylcarbene<sup>a</sup>

	3,3-dimethyldiazirine						dimethylcarbene						
	vertical		FC minima		intermediates		vertical		FC minima		intermediates		
R <sub>0</sub>	<sup>1</sup> A <sub>1</sub>	0.0					P <sub>0</sub>	<sup>1</sup> A <sub>1</sub>	0.40				
<sup>3</sup> R <sub>1</sub> ( <sup>3</sup> n <sub>z</sub> π*)	<sup>3</sup> B <sub>1</sub>	3.99	<sup>3</sup> R <sub>1</sub>	3.79	TS <sub>0</sub>	0.90	<sup>3</sup> P <sub>1</sub> ( <sup>3</sup> np <sub>y</sub> )	<sup>3</sup> B <sub>2</sub>	1.74	<sup>3</sup> P <sub>1</sub>	1.24	TS <sub>0</sub> '	1.50
<sup>3</sup> R <sub>2</sub> ( <sup>3</sup> n <sub>z</sub> σ*)	<sup>3</sup> B <sub>2</sub>	4.06			TR	2.70	P <sub>1</sub> ( <sup>1</sup> np <sub>y</sub> )	<sup>1</sup> B <sub>2</sub>	2.88	P <sub>1</sub>	2.17		
R <sub>1</sub> ( <sup>1</sup> n <sub>z</sub> π*)	<sup>1</sup> B <sub>1</sub>	4.24	R <sub>1</sub>	4.03	R <sub>3</sub>	3.83						propene	
R <sub>2</sub> ( <sup>1</sup> n <sub>z</sub> σ*)	<sup>1</sup> B <sub>2</sub>	5.27										P <sub>0</sub> '	-1.22
<sup>3</sup> R <sub>3</sub> ( <sup>3</sup> n <sub>z</sub> W*)	<sup>3</sup> A <sub>1</sub>	5.97											

<sup>a</sup> Relative energies for product states P are given as:  $\Delta E = E_p + E_{N_2} - E_{R_0}$ .

(DM) the HOMO is nonbonding (n), the next lower one a π MO with a nodal plane perpendicular to the molecular plane. The virtual MO's appear in increasing sequence as σ\*, π\*, n\*, and σ\*. In 2-diazoacetaldehyde we find the following MO situation. The two highest occupied MO's are nonbonding. The lower one of the two is a n<sub>o</sub> localized at oxygen. The HOMO (n) has its largest density at the α carbon. The LUMO is of σ\* type and corresponds to the one of DM. Two antibonding π\* MO's follow which are concentrated in the NN bond. We denote the one perpendicular to the molecular plane by π\*<sub>x</sub>, the other one by π\*<sub>y</sub>. The next virtual MO σ\*<sub>2</sub> has a topology similar to the LUMO. Therefore we have deleted it from Figure 3.

**3.2. Analysis of the Optical Spectra.** Now we want to analyze the optical spectra in the framework of the preceding considerations. The calculated excitation energies are presented in Tables I–III. The following notation is used. On the ground-state hypersurface S<sub>0</sub>, singlet states are denoted by R<sub>0</sub> for the reactants, P<sub>0</sub> (P<sub>0</sub>', etc.) for the products and TS<sub>0</sub> (TS<sub>0</sub>', etc.) for the transition states. On the excited singlet hypersurfaces S<sub>1</sub>, S<sub>2</sub>, ..., the reactants are denoted by R<sub>1</sub>, R<sub>2</sub>, ..., the product by P<sub>1</sub>, P<sub>2</sub>, ..., the intermediates by I<sub>1</sub>, I<sub>2</sub>, ..., and transitions to the R<sub>0</sub> surface, which are not originating from intermediates, by TR. The triplet states are denoted correspondingly by <sup>3</sup>R<sub>1</sub>, <sup>3</sup>R<sub>2</sub>, ..., <sup>3</sup>P<sub>1</sub>, ..., <sup>3</sup>I<sub>1</sub>, ...

**3.2.1. Spectra of Diazirine and Diazomethane.** First we compare the UV absorption of diazirine with our calculated excitation energies (Table I). The calculated heat of reaction of 1.84 eV from diazirine to diazomethane compares with the experimental value of 1.30 eV.<sup>26</sup> This molecule shows a structured long wave absorption band with a first vibronic transition at 320 nm (3.88 eV) and a stronger band below 220 nm (6.2 eV). In agreement with experiment<sup>23–25</sup> and ab initio studies,<sup>14–17</sup> we find a <sup>1</sup>n<sub>z</sub>π\* (<sup>1</sup>B<sub>1</sub>) transition at 4.59 eV. In the strong absorption region at 200 nm mentioned by Hoffmann<sup>18</sup> and Kirmse,<sup>6</sup> we find a <sup>1</sup>n<sub>z</sub>σ\*

(<sup>1</sup>B<sub>2</sub>) transition at 6.75 eV. Below the <sup>1</sup>B<sub>2</sub> state, there exist another four triplet states in the sequence <sup>3</sup>n<sub>z</sub>π\* (<sup>3</sup>B<sub>1</sub>), <sup>3</sup>ππ\* (<sup>3</sup>B<sub>2</sub>), <sup>3</sup>n<sub>z</sub>σ\* (<sup>3</sup>B<sub>2</sub>), and <sup>3</sup>n<sub>z</sub>W\* (<sup>3</sup>A<sub>1</sub>) (see Table I).

In the following we want to compare the spectral transitions of diazomethane obtained in this work with the values from absorption spectra. DM shows absorption between 460 and 320 nm, 260 and 200 nm, and from 190 nm.<sup>27–29</sup> The SINDO1 calculations yield a first <sup>1</sup>nσ\*<sub>1</sub> (<sup>1</sup>B<sub>2</sub>) transition at 2.81 eV and a second forbidden <sup>1</sup>nπ\* (<sup>1</sup>A<sub>2</sub>) transition at 3.49 eV. These two states correspond with the maxima at 452.5 nm (2.74 eV) and 395 nm (3.14 eV). Other calculations<sup>14–17</sup> did not investigate the experimentally assigned shoulder at 2.74 eV. For the second absorption region, Herzberg<sup>30</sup> assigns a maximum at 217.5 nm (5.7 eV). Here we find two excitations close together. The first is at 5.75 eV and mainly due to a <sup>2</sup>nσ\*<sub>1</sub> double excitation with a small 10% <sup>1</sup>nn\* admixture. Goddard<sup>14</sup> assigns this <sup>1</sup>A<sub>1</sub> state at 5.9 eV. The second excitation appears at 5.91 eV. This <sup>1</sup>B<sub>1</sub> state is generated by a <sup>1</sup>nσ\*<sub>2</sub> excitation. In this region there are also four triplet states in the sequence <sup>3</sup>nσ\*<sub>1</sub> (<sup>3</sup>B<sub>2</sub>) < <sup>3</sup>nn\* (<sup>3</sup>A<sub>1</sub>) < <sup>3</sup>nπ\* (<sup>3</sup>A<sub>2</sub>) < <sup>3</sup>nσ\*<sub>2</sub> (<sup>3</sup>B<sub>2</sub>). The region at 190 nm is mainly determined by Rydberg states as shown by Goddard. Such transitions cannot be investigated by minimal basis sets, and we exclude them from further consideration. This has no unfavorable consequences since the photochemistry of the studied molecules is initiated under conservation of the main quantum number as we shall show below.

**3.2.2. Spectrum of 3,3-Dimethyldiazirine and 2-Diazopropane.** We now consider the vertical spectrum of 3,3-dimethyldiazirine. The first absorption region appears between 290 and 360 nm

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Table III. Calculated Relative Energies (eV) of Excited States of 3-Formyldiazirine and 2-Diazoacetaldehyde<sup>a</sup>

3-formyldiazirine					2-diazoacetaldehyde				
vertical		FC minima	intermediates		vertical		FC minima		
R <sub>0</sub>	<sup>1</sup> A'	0.0			P <sub>0</sub>	<sup>1</sup> A'	0.0		
<sup>3</sup> R <sub>1</sub> ( <sup>3</sup> n <sub>0</sub> πCO*, <sup>3</sup> n <sub>0</sub> π <sub>NN</sub> *)	<sup>3</sup> A''	4.21	<sup>3</sup> R <sub>1</sub> ( <sup>3</sup> A'')	4.16	TS <sub>0</sub>	1.59	<sup>3</sup> P <sub>1</sub> ( <sup>3</sup> nσ <sub>1</sub> *)	<sup>3</sup> A''	1.67
R <sub>1</sub> ( <sup>1</sup> n <sub>0</sub> πCO*, <sup>1</sup> n <sub>0</sub> π <sub>NN</sub> *)	<sup>1</sup> A''	4.71	R <sub>1</sub> ( <sup>1</sup> A'')	4.45	<sup>3</sup> I <sub>1</sub>	2.57	P <sub>1</sub> ( <sup>1</sup> nσ <sub>1</sub> *)	<sup>1</sup> A''	3.14 (3.45)
<sup>3</sup> R <sub>2</sub> ( <sup>3</sup> n <sub>N</sub> π <sub>NN</sub> *, <sup>3</sup> n <sub>N</sub> πCO*)	<sup>3</sup> A'	4.78			I <sub>1</sub>	3.79	<sup>3</sup> P <sub>2</sub> ( <sup>3</sup> nπ <sub>x</sub> *)	<sup>3</sup> A'	3.96
<sup>3</sup> R <sub>3</sub> ( <sup>3</sup> n <sub>N</sub> σ*)	<sup>3</sup> A''	4.84					<sup>3</sup> P <sub>3</sub> ( <sup>3</sup> nπ <sub>y</sub> *)	<sup>3</sup> A''	4.61
R <sub>2</sub> ( <sup>1</sup> n <sub>N</sub> π <sub>NN</sub> *, <sup>1</sup> n <sub>N</sub> πCO*)	<sup>1</sup> A'	5.17	R <sub>2</sub> ( <sup>1</sup> A)	4.75			P <sub>2</sub> ( <sup>1</sup> nπ <sub>y</sub> *)	<sup>1</sup> A''	4.75
<sup>3</sup> R <sub>4</sub> ( <sup>3</sup> n <sub>0</sub> σ*)	<sup>3</sup> A'	5.41					<sup>3</sup> P <sub>4</sub> ( <sup>3</sup> n <sub>0</sub> σ <sub>1</sub> *)	<sup>3</sup> A'	5.08
<sup>3</sup> R <sub>5</sub> ( <sup>3</sup> n <sub>N</sub> πCO*, <sup>3</sup> n <sub>N</sub> π <sub>NN</sub> *)	<sup>3</sup> A'	6.41					<sup>3</sup> P <sub>5</sub> ( <sup>3</sup> nσ <sub>2</sub> *)	<sup>3</sup> A''	5.09
R <sub>3</sub> ( <sup>1</sup> n <sub>N</sub> σ*)	<sup>1</sup> A''	6.43					P <sub>3</sub> ( <sup>1</sup> nπ <sub>x</sub> *, <sup>1</sup> n <sub>0</sub> σ <sub>1</sub> *)	<sup>1</sup> A'	5.41 (4.56)
							<sup>3</sup> P <sub>6</sub> ( <sup>3</sup> nπCO*)	<sup>3</sup> A'	5.65
							P <sub>4</sub> ( <sup>1</sup> nσ <sub>2</sub> *)	<sup>1</sup> A''	5.89 (5.0)
							P <sub>5</sub> ( <sup>1</sup> n <sub>0</sub> σ <sub>1</sub> *, <sup>1</sup> nπ <sub>x</sub> *)	<sup>1</sup> A'	6.83 (>6.2)

<sup>a</sup> E<sub>P<sub>0</sub></sub> - E<sub>R<sub>0</sub></sub> = 1.24 eV. Energies are relative to the corresponding ground state R<sub>0</sub>, P<sub>0</sub> with experimental values in parentheses.

(4.28–3.45 eV) with numerous bands. The next maximum is below 190 nm (6.53 eV).<sup>31,32</sup> Our calculations yield two singlet transitions (see Table II) 1.03 eV apart. The first is a <sup>1</sup>n-π\* (<sup>1</sup>B<sub>1</sub>) transition, the second a <sup>1</sup>n-σ\* (<sup>1</sup>B<sub>2</sub>) transition. These two allowed transitions can be assigned to the absorption between 290 and 360 nm. Below 6 eV there are also the three triplet states <sup>3</sup>n-π\* (<sup>3</sup>B<sub>1</sub>), <sup>3</sup>n-σ\* (<sup>3</sup>B<sub>2</sub>), and <sup>3</sup>n-W\* (<sup>3</sup>A<sub>1</sub>). There are no further singlet transitions below the calculated ionization potential (IP) of 8.87 eV. We assume therefore that the 190 nm band is generated by Rydberg excitations. We see that this spectrum shows significant differences to the one of diazirine. In the dimethyl-substituted three-membered ring, the vertical <sup>1,3</sup>n-σ\* states are lowered by more than 1 eV. We see also a red shift, but less pronounced, for the n-π\* excitations. The <sup>3</sup>ππ\* (<sup>3</sup>B<sub>2</sub>) state appears only at 6.67 eV.

2-Diazopropane shows an absorption at λ<sub>max</sub> ≈ 500 nm (ε ≈ 2)<sup>33,34</sup> with a half-life of about 3 h at 273 K in ether solution. Heilbronner and Martin<sup>35</sup> discuss the photoelectron spectrum of the molecule under the assumption of C<sub>2v</sub> symmetry and determine the first ionization potential at 7.88 eV. From our calculations we conclude that the free molecule is metastable in this geometry. The SINDO1 results yield an ionization potential of 6.82 eV and a first long wave <sup>1</sup>nσ\* transition at 1.97 eV (612 nm). These values are comparable with the experimental ones in polar solvents. The next measurable absorption should be in the UV region. We obtain there a <sup>1</sup>nπ\* transition at 3.92 eV (308 nm). We find a shallow minimum of a few kcal/mol in C<sub>s</sub> symmetry in a trans arrangement. The ionization potential is 7.72 eV.

**3.2.3. Spectrum of 3-Formyldiazirine and of 2-Diazoacetaldehyde.** Finally we analyze the vertical transitions of 3-formyldiazirine and of 2-diazoacetaldehyde. Experimental values for the latter are given by Arnold et al.<sup>36</sup> We present the calculated energies in Table III. We see that the CO substituent influences the type of excitation through the topology of the MO's. The first two singlet transitions in FDI are no longer due to local excitations. They are mixtures of two different nπ\* transitions. R<sub>1</sub> lies at 4.71 eV and the corresponding R<sub>2</sub> at 5.17 eV. The two highest occupied MO's are therefore almost equally involved in this absorption region. The next singlet R<sub>3</sub> at 6.43 eV is of local nature and results from a <sup>1</sup>n<sub>N</sub>σ\* transition. It corresponds also energetically to the R<sub>2</sub> of diazirine. The five triplet states below R<sub>3</sub> have either local nσ\* or mixed nonlocal nπ\* character. Apart from the accumulation of states between 4.2 and 6.4 eV due to the CO group, this spectrum is comparable to the one of diazirine. It can be separated into two absorption regions. The first appears below 5.2 eV, the second at 6.4 eV. The accumulation of states just mentioned results in considerably more complicated photophysical and photochemical processes.

The UV spectrum of 2-diazoacetaldehyde obtained in polar solvents shows absorption at 3.45 eV (360 nm), 4.56 (272), 5.0 (248), and below 200.<sup>36</sup> We calculate a <sup>1</sup>nσ\*<sub>1</sub> transition at 3.14 eV analogous to the <sup>1</sup>nσ\*<sub>1</sub> (2.81 eV) of diazomethane which can be attributed to the absorption at 3.45 eV. In addition we find two absorptions, <sup>1</sup>nσ\*<sub>2</sub> at 5.89 eV and a mixed (<sup>1</sup>nπ\*<sub>x</sub>, <sup>1</sup>n<sub>0</sub>σ\*<sub>1</sub>) at 5.41 eV, which correspond to the maxima at 272 and 248 nm. An additional transition <sup>1</sup>nπ\*<sub>y</sub> appears at 4.75 eV with an oscillator strength by three orders of magnitude smaller than for the other excitations. Because of this small oscillator strength we cannot extract this transition from the experimental UV spectrum.<sup>36</sup> Finally we find a mixed (<sup>1</sup>nπ\*<sub>x</sub>, <sup>1</sup>n<sub>0</sub>σ\*<sub>1</sub>) excitation at 6.83 eV in the absorption region below 200 nm. Below the <sup>1</sup>nσ\*<sub>2</sub> transition there exist six vertical triplet states (see Table III). It is remarkable that the first three singlets in the aldehyde are of local nature, different from the situation in the cyclic isomer.

#### 4. Equilibrium Geometries

Before the discussion of the reaction of the diazirines, we consider first the equilibrium geometries. The most important internal coordinates are given in Table IV–VI. In addition we have collected the ionization potentials (IP), dipole moments (μ), and the relevant bond orders.<sup>37,38</sup>

**4.1. Diazirine and Its Products.** We find C<sub>2v</sub> symmetry for diazirine with an NN bond length of 1.174 Å and NC bond lengths of 1.440 Å (see Table IV). The Franck-Condon (FC) minima R<sub>1</sub> and <sup>3</sup>R<sub>1</sub> are also of C<sub>2v</sub> symmetry and differ only slightly in their geometry. Compared to R<sub>0</sub>, their NN bond is expanded by 0.019 and 0.02 Å, respectively, and their NC bond by 0.034 and 0.038 Å, respectively. The dipole moments are increased by 3.25 and 3.22 D, respectively. This corresponds to the expected influence nπ\* excitation on the geometry of the molecule. Outside of the FC zone there is a minimum <sup>3</sup>R<sub>2</sub> which originates from a vertical ππ\* transition above the ground state.

There are two intermediates I<sub>1</sub>' and <sup>3</sup>I<sub>1</sub>' with NNC angles of 115.9 and 120.0° on the singlet and triplet hypersurfaces, respectively, which are passed during the isomerization. <sup>3</sup>I<sub>1</sub>' is located in a diradical region. For such a diradical the ground state and the triplet state are almost degenerate. States are zwitterionic if the ionic components dominate in the wave function. Details of this definition were given previously.<sup>39–41</sup> In agreement with experiment<sup>30</sup> we find the product diazomethane (P<sub>0</sub>') in C<sub>2v</sub> symmetry. In the FC zone there is also the planar minimum P<sub>2</sub>' which has a NN bond expanded by 0.052 Å and NC bond contracted by 0.065 Å compared to DM. Methylene is obtained as a dissociative product. We find a CH bond length of 1.059 Å and an HCH angle of 135.1° for the triplet ground state <sup>3</sup>P<sub>0</sub>'; the

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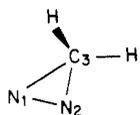
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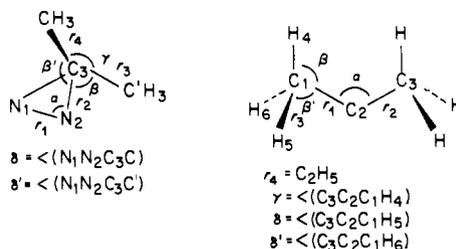
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**Table IV.** Calculated Bond Orders, Bond Lengths (Å), Bond and Dihedral Angles (deg), Ionization Potentials IP (eV), and Dipole Moments  $\mu$  (Debye) of Ground and Excited States of Diazirine and Diazomethane

	bond order			geometry							IP	$\mu$
	NN	N <sub>1</sub> C	N <sub>2</sub> C	r <sub>NN</sub>	r <sub>NC</sub>	$\phi_{N_1N_2C_3}$	$\phi_{HCH}$	$\phi_{N_1NCH}$	$\phi_{N_2NCH}$			
R <sub>0</sub>	2.28	1.25	1.25	1.174	1.440	65.9	114.6	-105.0	105.0	10.62 (10.18°)	0.47	
R <sub>1</sub>	2.00	1.01	1.01	1.193	1.474	66.9	113.5	-105.0	105.0		3.72	
<sup>3</sup> R <sub>1</sub>	2.00	1.02	1.02	1.194	1.468	66.0	113.5	-105.0	105.0		3.69	
<sup>3</sup> R <sub>2</sub>	1.64	1.27	1.27	1.289	1.446	63.7	117.8	-95.0	115.0		3.50	
TR	2.96	0.22	0.22	1.090	2.300	76.3	131.5	-113.5	113.5		1.55	
I <sub>1</sub> '	2.65	-0.42	1.16	1.110	1.458	115.9	124.6	-90.0	89.4		1.66	
<sup>3</sup> I <sub>1</sub> '	2.47	0.19	1.22	1.136	1.385	120.0	113.3	-103.0	103.5		1.87	
P <sub>0</sub> '	2.60		1.63	1.128	1.345	180.0	126.0	-90.0	90.0	8.15 (9.00°)	0.38	
P <sub>2</sub> '	2.07		1.84	1.180	1.280	180.0	118.8	-90.0	90.0		3.59	

<sup>a</sup> Reference 26.

**Table V.** Calculated Bond Orders, Bond Lengths (Å), Bond and Dihedral Angles (degrees), Ionization Potentials IP (eV), and Dipole Moments  $\mu$  (Debye) of Ground and Excited States of 3,3-Dimethyldiazirine, 2-Diazopropane, and Dimethylcarbene

	bond order			geometry											IP	$\mu$
	NN	N <sub>1</sub> C <sub>3</sub>	N <sub>2</sub> C <sub>3</sub>	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>	$\alpha$	$\beta$	$\beta'$	$\gamma$	$\delta$	$\delta'$			
R <sub>0</sub>	2.32	1.16	1.16	1.166	1.488	1.561	1.561	66.9	116.9	116.9	121.3	-102.2	102.2	8.87	0.59	
R <sub>1</sub>	2.00	0.95	0.95	1.189	1.535	1.538	1.538	67.2	116.7	116.7	121.3	-103.1	102.2		5.03	
<sup>3</sup> R <sub>1</sub>	2.00	0.96	0.96	1.192	1.527	1.541	1.541	67.0	116.7	116.7	121.1	-103.9	101.9		4.96	
TR	2.96	0.25	0.25	1.091	2.20	1.461	1.461	75.6	112.0	112.0	134.6	-95.7	95.7		0.40	
TS <sub>0</sub>	2.89	0.48	2.0	1.098	2.0	1.508	1.508	74.1	111.2	111.2	117.9	-67.0	66.5		2.17	
DIP(C <sub>2v</sub> )	2.74		1.34	1.114	1.432	1.520	1.520	180.0	112.8	112.8	134.4	-90.0	90.0	6.82	0.60	
DIP(C <sub>s</sub> )	2.89		0.79	1.103	1.594	1.520	1.520	159.5	107.1	107.1	118.6	-61.5	61.5	7.72	2.21	

	bond order			geometry											IP	$\mu$
	C <sub>1</sub> C <sub>2</sub>	C <sub>2</sub> C <sub>3</sub>	C <sub>1</sub> H <sub>3</sub>	r <sub>1</sub>	r <sub>2</sub>	r <sub>3</sub>	r <sub>4</sub>	$\alpha$	$\beta$	$\beta'$	$\gamma$	$\delta$	$\delta'$			
P <sub>0</sub>	1.42	1.42	0.97	1.453	1.453	1.094	2.071	124.5	119.8	104.3	0.0	122.1	-122.1	8.79	1.81	
P <sub>1</sub>	1.55	1.55	0.95	1.452	1.452	1.086	2.025	146.6	109.3	108.5	-5.3	114.8	-125.3		1.37	
<sup>3</sup> P <sub>1</sub>	1.53	1.53	0.95	1.465	1.465	1.083	2.068	141.4	110.1	107.6	-3.6	116.4	-123.6		1.40	
TS <sub>0</sub> '	1.76	1.29	0.52	1.357	1.497	1.459	1.227	127.7	126.2	51.5	-4.3	113.4	-172.6		2.38	

respective values for the singlet state <sup>1</sup>P<sub>0</sub> are 1.089 Å and 112°.

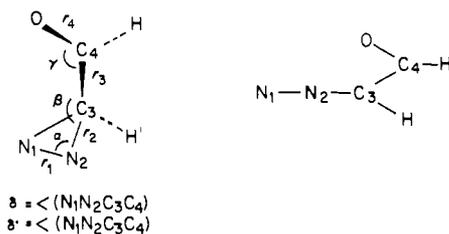
**4.2. 3,3-Dimethyldiazirine and Its Products.** The geometrical data are collected in Table V. DDI has C<sub>2v</sub> symmetry in its ground-state equilibrium R<sub>0</sub>. The NN bond length is insignificantly reduced by 0.008 Å by the substitution compared to diazirine, but the NC bond length is expanded by 0.048 Å. The ionization potential is reduced by 1.75 eV; the dipole moment is slightly increased by 0.12 D.

The FC minima R<sub>1</sub> and <sup>3</sup>R<sub>1</sub> on the nπ\* surfaces show NN and NC bonds with expansions of the same magnitude as in diazirine as well as a dipole moment increased by about 4.4 D. The dissociation on the lowest excited singlet surface passes through a region of C<sub>s</sub> symmetry which includes a point TR with NC bond lengths of 2.2 Å and other coordinates fully optimized. The significance of TR is discussed below. Here the bond orders are reduced to 0.25 and the dipole moment is 0.4 D.

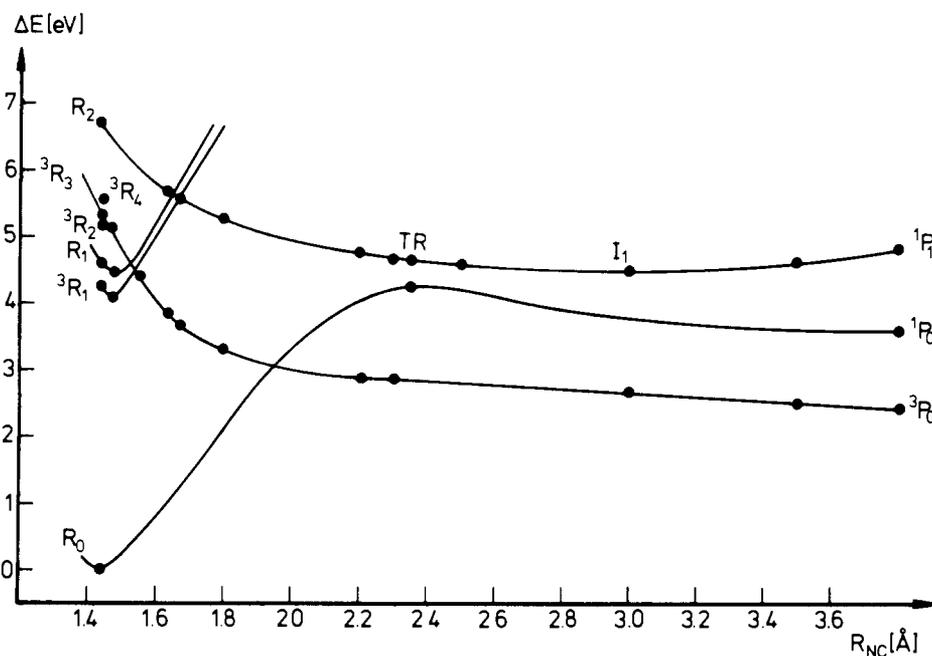
The product is dimethylcarbene with CC bond lengths of 1.453 Å and a CCC angle of 124.5°. The minimum <sup>3</sup>P<sub>1</sub> of the first triplet state of C(CH<sub>3</sub>)<sub>2</sub> has the corresponding values of 1.465 Å and 141.4°, but in C<sub>2</sub> symmetry. We find also a P<sub>1</sub> minimum with internal coordinates r<sub>CC</sub> = 1.452 Å and  $\phi_{CCC}$  = 146.6° in C<sub>2</sub> symmetry.

The first thermal transition state TS<sub>0</sub> appears at NC distances of 2.0 Å with bond orders of 0.48 and a dipole moment of 2.17 D. The methyl groups are turned by 35° out of the symmetry plane, which was originally orthogonal to the NNC ring. The rearrangement of singlet carbene (P<sub>0</sub>) to propene (P<sub>0</sub>') by hydrogen migration takes place thermally via the transition state TS<sub>0</sub>' with a nonsymmetrical CHC arrangement. The CH lengths are 1.459 and 1.227 Å. Both transition states are fully optimized and characterized by one negative root of the force constant matrix.

**4.3. 3-Formyldiazirine and Its Products.** The data of 3-formyldiazirine are collected in Table VI. We see that the CO substitution significantly increases the number of states compared with those of the previous three-membered rings. FDI has C<sub>s</sub> symmetry. The CO group points in the direction of the ring. The FC minima R<sub>1</sub> and <sup>3</sup>R<sub>1</sub> have almost identical geometry. The dominating n<sub>O</sub>π\*<sub>CO</sub> excitation expands the CO bond as expected, by 0.04 Å. The remaining structure and the dipole moment are almost unchanged compared to R<sub>0</sub>. The additional excitation n<sub>O</sub>π\*<sub>NN</sub> contracts the NN and NC bonds. Outside of the FC zone there is another minimum R<sub>2</sub> without a corresponding state on the triplet surfaces. The dominating excitation here is n<sub>N</sub>π\*<sub>NN</sub> which gives rise to a NN bond expansion by 0.042 Å. Simulta-

**Table VI.** Calculated Bond Orders, Bond Lengths (Å), Bond and Dihedral Angles (degrees), Ionization Potentials IP (eV), and Dipole Moments  $\mu$  (Debye) of Ground and Excited States of 3-Formyldiazirine and 2-Diazoacetaldehyde

	bond order				geometry												IP	$\mu$
	$N_1N_2$	$N_1C_3$	$N_2C_3$	$C_3C_4$	$r_1$	$r_2$	$r_3$	$r_4$	$\alpha$	$\beta$	$\gamma$	$\delta$	$\delta'$					
$R_0$	2.35	1.17	1.17	1.28	1.163	1.477	1.526	1.215	66.8	121.7	127.5	-105.8	102.1	9.87	2.12			
$R_1$	2.19	1.22	1.22	1.24	1.156	1.456	1.533	1.255	66.6	119.7	125.0	-104.4	103.2		2.33			
$R_2$	2.03	0.76	1.15	1.35	1.205	1.465	1.515	1.197	74.1	122.4	126.0	-104.0	99.4		4.50			
$^3R_1$	2.19	1.22	1.22	1.24	1.156	1.456	1.533	1.255	66.6	119.7	125.0	-104.4	103.2		2.33			
$^3I_1$	2.62	0.01	1.14	1.38	1.108	1.437	1.513	1.207	141.9	127.0	124.3	132.8	-54.4		2.65			
$I_1$	2.63	0.13	1.05	1.43	1.115	1.450	1.481	1.212	136.1	122.7	126.3	128.0	-48.2		2.65			
$TS_0$	2.86	0.14	0.68	1.39	1.102	1.63	1.463	1.219	115.9	110.0	131.6	117.7	-10.0		3.21			
$P_0$	2.77	0.0	1.30	1.46	1.110	1.424	1.466	1.220	180.0	119.2	131.0	180.0	0.0	8.33	3.08			
$P_2$	2.25	0.0	1.62	1.34	1.147	1.329	1.508	1.206	179.5	125.4	127.7	180.0	0.0		4.09			
$^3P_1$	2.87	0.0	0.74	1.38	1.094	1.66	1.501	1.201	179.5	124.9	126.7	175.6	-5.1		1.24			
$^3P_2$	2.31	0.0	1.30	1.50	1.158	1.356	1.470	1.211	171.0	122.5	125.9	174.0	-8.3		3.49			

**Figure 4.** Potential curves for the synchronous ring opening of diazirine on the  $R_2$  and  $^3R_3$  surfaces: ●, points of optimized geometry.

neously a NNC angle is increased to  $74.1^\circ$ , which causes a reduction of the bond order to 0.76 from 1.17 in  $R_0$ . The dipole moment is increased to 4.5 D by the  $n_{NN}\pi^*_{NN}$  excitation. The admixed  $n_{NN}\pi^*_{CO}$  excitation enforces in addition a small contraction of the CO bond by 0.018 Å. During the isomerization the minima  $I_1$  and  $^3I_1$  appear on the lowest singlet and triplet surfaces at ring opening angles of  $\phi_{NNC} = 136.1$  and  $141.9^\circ$ . The intermediate  $^3I_1$  is not a diradical. Geometries, dipole moments, and bond orders are of comparable magnitude in both states. At  $\phi_{NNC} = 115.9^\circ$  we find the thermal transition state  $TS_0$  with a further weakened NC bond compared to  $I_1$  and  $^3I_1$ . The NC bond orders are 0.14 and 0.68. Also all bond lengths and angles are different, but the arrangement of the atoms in space is comparable to the one in  $I_1$  and  $^3I_1$ . The last three states have  $C_1$  symmetry.

We find planar 2-diazoacetaldehyde in  $C_s$  symmetry as the main product  $P_0$ . Above  $P_0$  there appears the minimum  $P_2$  in the FC zone caused by a  $n\pi^*$  excitation. It is slightly nonlinear; the NN bond is expanded to 1.147 Å by the excitation. Also in the FC zone is the minimum  $^3P_2$  with a NN bond length of 1.158 Å and

a NN angle of  $171^\circ$ . The first triplet surfaces of  $P_0$  has a  $^3P_1$  minimum with a NC bond expanded to 1.66 Å.

## 5. Potential Hypersurfaces and Reaction Mechanisms

### 5.1. Diazirine.

Experiments show that methylene as well as diazomethane appear in the photolysis of diazirine. There are doubts about DM as the primary product.<sup>4,6</sup>

We take Figure 4 as a starting point for a discussion of this question. It shows a two-dimensional cut through the hypersurfaces which describe the reaction diazirine ( $h\nu$ )  $\rightarrow$   $^1,^3CH_2 + N_2$ . Above the ground state of diazirine there are two minima  $^3R_1$  and  $R_1$  in the FC zone. For technical reasons, we could not include the third minimum  $^3R_2$  ( $^3\pi\pi^*$ ) in the figure because it is located outside of the FC zone with an expanded NN bond.

The excitation from the nonbonding HOMO into the virtual  $\sigma^*$  MO weakens both NC bonds. This leads to the repulsive singlet state  $R_2$ . On its surface spontaneous dissociation under conservation of  $C_{2v}$  symmetry takes place. During this process a symmetry-allowed crossing with the  $R_1$  ( $^1n\pi^*$ ) surface occurs. The

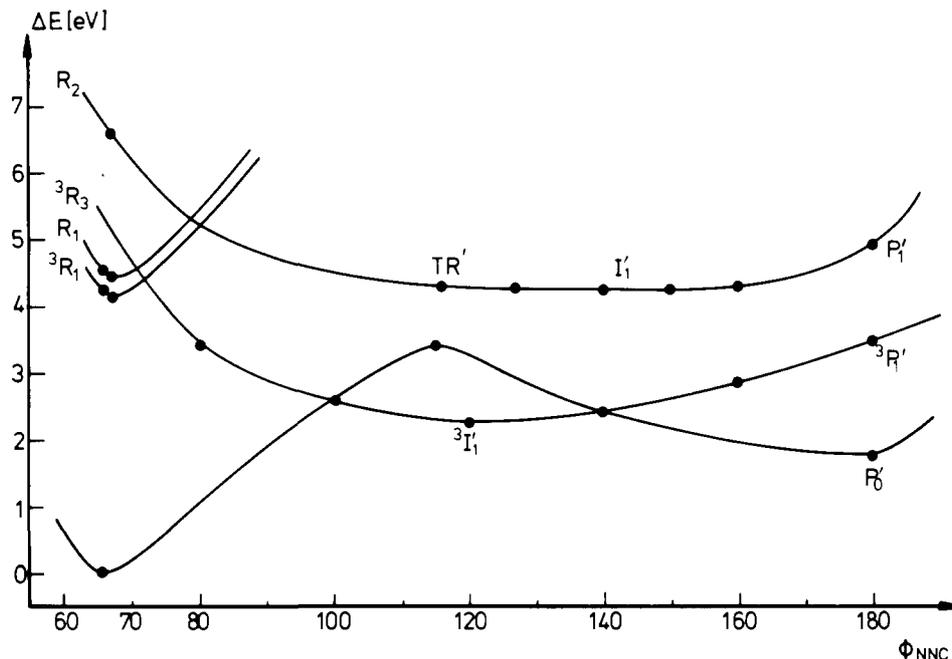


Figure 5. Potential curves for the photochemical isomerization of diazirine to diazomethane: ●, points of optimized geometry.

crossing point of  ${}^1B_2$  and  ${}^1B_1$  appears at 5.65 eV. The  $R_2$  state passes through a rather flat minimum  $I_1$  at a  $N_1C_3, N_2C_3$  distance between 2.5 and 3.0 Å. Vertically below  $TR$  at 2.35 Å the  $R_0$  surface appears with an energy of 4.25 eV. The calculated distance between both surfaces is here minimal (0.35 eV). This enforces a radiationless transition which leads to  ${}^1CH_2({}^1A_1) + N_2({}^1\Sigma_g^+)$ . We address ourselves to this transition again at the end of this section. The  $R_2$  surface ends in the geometry  ${}^1P_1$  of the first excited singlet methylene state  ${}^1CH_2({}^1B_2)$  plus  $N_2({}^1\Sigma_g^+)$ .

The excitation into the  $R_1$  state may not lead immediately to a photochemical process. Only a further thermal excitation by less than 1 eV would enable the reaction under conservation of spin multiplicity. This process should circumvent the conical intersection. The symmetry must be lower than  $C_s$  and should involve a rotation of the methylene group together with the breaking of one CN bond. Difficulties with the topology of the wave function near the conical intersection have prevented us from locating a transition structure as a first-order saddle point on the first excited singlet surface. However, intersystem crossing (ISC) to the triplet states  ${}^3R_1, {}^3R_2$ , and  ${}^3R_3$  which appear close to the low-lying vibrational modes seems more probable for low-energy excitation under the assumption that the barrier between  $R_1$  and  $R_2$  is close to the conical intersection. The process  $R_1 \rightsquigarrow {}^3R_2$  is least likely since it requires an intrashell  $\pi \rightarrow n$  excitation. The process  $R_1 \rightsquigarrow {}^3R_1$  should be favorable since the spin flip can be compensated by a spatial reorientation of the excited electron by  $90^\circ$ . The transition  $R_1 \rightsquigarrow {}^3R_3$  should be most favorable since both electrons of equal spin have maximum separation. The  ${}^3R_3({}^3n\sigma^*)$  surface is repulsive as expected and enables dissociation under conservation of  $C_{2v}$  symmetry to methylene in its ground-state  ${}^3CH_2$ .

At this point we wish to insert the following consideration. In the region in which we expect the radiationless transition from the singly excited singlet  $R_2$  to  $R_0$ , there appears the HOMO-LUMO crossing required by the Woodward-Hoffmann (WH) rules<sup>42</sup> for this dissociation. Here the ground state correlates with a doubly excited state which is higher by about 2 eV. We have designated the position, where the  $R_2$  and  $R_0$  surfaces are close, with  $TR$ . This means transition region. Here the radiationless transition from a singly excited singlet to the ground state can be initiated due to HOMO-LUMO degeneracy. This process is essentially different from the notion of conical intersection. In

the latter case there is symmetry-allowed crossing of, e.g., a doubly excited singlet and the ground state or two singly excited energy hypersurfaces. We shall discuss this process of radiationless transition later for the case of dissociation of 3,3-dimethyldiazirine. Finally we have to clarify the question how diazomethane can be obtained photolytically. Our calculations show on one hand that the free molecule diazirine dissociates on the  $n\sigma^*$  surfaces  $R_2$  or  ${}^3R_3$  under conservation of  $C_{2v}$  symmetry and on the other hand that the  $n\pi^*$  states are primarily photochemically irrelevant. In consequence DM can only be generated if the symmetry is lowered during the dissociative process by activation of nontotally symmetric vibrations. To simulate these processes we have subjected those energy hypersurfaces to energy variations, which result from an expansion of only one NC bond. The results are presented in Figure 5. The  $R_2$  ( ${}^1n\sigma^*$ ) surface shows the very flat minimum  $I_1'$  at NC angles between 115 and  $150^\circ$  under the restriction of asymmetric ring opening. At  $115.9^\circ$  there is a symmetry-conditioned avoided HOMO-LUMO crossing. We have designated the significant point in the region, where the transition from  $R_2$  to  $R_0$  can occur, by  $TR'$ . By this transition diazomethane can be obtained in its ground state  $P_0'$ .

Similar to the  $R_2$  surface, the  ${}^3n\sigma^*$  state  ${}^3R_3$  passes at  $\phi_{NNC} = 120^\circ$  through the diradicaloid minimum  ${}^3I_1'$ . By definition<sup>37-39</sup> we should not call this stationary state a diradical. But Figure 5 shows that the singlet crosses the triplet at  $\phi_{NNC} = 100$  and  $140^\circ$  and the maximum separation is only 0.3 eV. We therefore call this region diradicaloid. Intersystem crossing from  ${}^3I_1'$  to  $R_0$  furnishes also the product  $P_0'$ . It is now clear that excitations of diazirine in the short wave absorption region generate primarily singlet methylene. By long wave absorption triplet methylene is generated as primary product. Diazomethane can only be in its ground state obtained from  $R_1$  by opening of one CN bond and reduction to  $C_1$  symmetry.

This information cannot be derived from the ab initio calculations by Devaquet et al.<sup>17</sup> since these authors did not investigate the photochemically dominating  $n\sigma^*$  excitations. Also we emphasize that it is necessary for the explanation of photochemical reaction mechanisms to optimize the geometry of excited states according to the energy variation principle for all relevant coordinates.

**5.2. 3,3-Dimethyldiazirine.** In the photolysis of 3,3-dimethyldiazirine studied by Frey and Stevens<sup>31</sup> in 1963 in the gas phase, propene is found as the main product. 2-Diazopropane (DIP) is not observed. The results agree with those found in the thermal decomposition of the ring.<sup>12</sup> Before we address ourselves

(42) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, 1971.

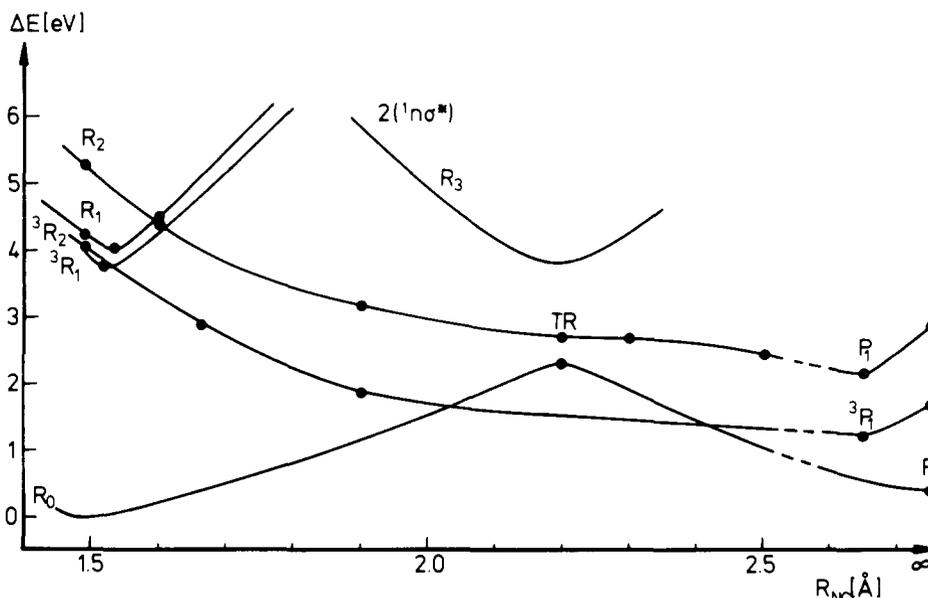


Figure 6. Potential curves for the photochemical dissociation of 3,3-dimethyldiazirine: ●, points of optimized geometry.

to the photochemistry of the three-membered ring we want to check the existence of the linear molecule by our calculations. The geometry of the planar DIP of  $C_{2v}$  symmetry is presented in Table V (line DIP). The calculated planar arrangement corresponds to a transition state on the energy hypersurface with the tendency to turn the methyl groups symmetrically out of the molecular plane and the outer N in the trans position. A shallow minimum of  $C_s$  symmetry appears at  $\phi_{\text{NNCC}} = 61.5$  and  $-61.5^\circ$  with a bond length  $R_{\text{NC}} = 1.6$  Å. The NC bond order is reduced from 1.34 in the planar ground state to 0.79. The related energy is 0.4 eV higher than that of the ring and 0.89 eV lower than that of the transition state. From this minimum a small barrier of a few kcal/mol leads to the completely dissociated product dimethylcarbene plus  $\text{N}_2$ . On the other hand, as experiments show,<sup>33</sup> 2-diazopropane exists in ether solution with a half-life of 3 h. From this measurement one would expect a deeper well depth. Yet the calculated small barrier makes it more understandable that only carbene and its rearrangement product can be generated in both photolysis and thermolysis of 3,3-dimethyldiazirine.

In the following we are concerned with the photochemistry of DDI with the help of Figure 6. As the diagram shows the photodissociation occurs qualitatively in analogy to that of diazirine (Figure 4). But we want to point out two essential differences. The repulsive  $R_2$  ( $1n\sigma^*$ ) state appears in DDI already at 5.27 eV. The  $R_1$ ,  $R_2$  crossing point is only 0.42 eV above the  $1n\pi^*$  minimum  $R_1$  and 0.2 eV above the first vertical excitation. Therefore a reaction can be initiated already by excitation of the lowest  $R_1$  vibrational modes by IC. ISC processes are negligible so that triplet carbene should not be observed.

Contrary to diazirine the  $1n\sigma^*$  surface shows no intermediate. We find the first minimum in the system  $\text{N}_2$  plus  $\text{C}(\text{CH}_3)_2$  ( $P_1$ ) in its first singlet state. When the point TR is reached at a NC distance of 2.2 Å, there is a minimal separation of 0.56 eV between the  $R_2$  and  $R_0$  surfaces. If a radiationless transition occurs from the  $R_2$  state at this point, the additional energy of 2 eV suffices to form a variety of products. This is confirmed by the experimental work of Frey and Stevens.<sup>31</sup>

We have also investigated the thermal reaction. The transition state  $\text{TS}_0$  for the ring cleavage again occurs symmetrically at NC distances of 2.1 Å with an activation energy  $E_a = 0.9$  eV (see Figure 7). The carbene formed afterwards has to supply an additional 1.10 eV to enable the hydrogen migration and to surpass the transition state  $\text{TS}_0'$ . A similar barrier of 1.17 eV was found by Csizmadia<sup>43</sup> for the methylcarbene  $\rightarrow$  ethylene reaction.

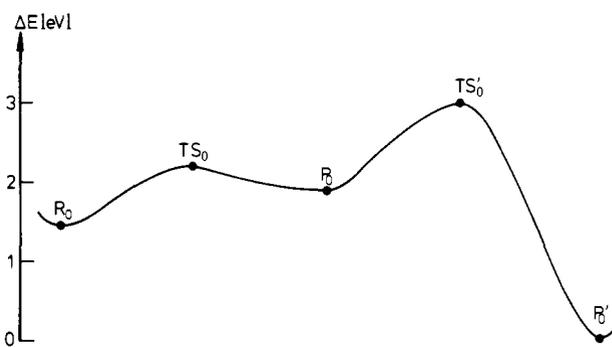


Figure 7. Potential curve for the thermal reaction of 3,3-dimethyldiazirine to propene.

However, Schaefer<sup>44</sup> suggests a barrier of 0.35 eV for such a rearrangement to obtain consistency with experimental findings. We feel that extensive configuration interaction is necessary to achieve this. We obtain propene as product. The total barrier is 1.5 eV which agrees well with the experimental result of 1.44 eV.<sup>12</sup>

In our perception, neither diradicals or zwitterions appear as transition states or intermediates in the thermally or photochemically induced dissociation of 3,3-dimethyldiazirine. In this conclusion we differ from Liu.<sup>4</sup> Finally we want to consider TR and  $\text{TS}_0$  in light of the Woodward-Hoffmann rules with the help of Figure 8. From the left part of the diagram we conclude that the totally symmetrical dissociation of dimethyldiazirine under conservation of orbital and molecular symmetry is forbidden. The  $n$ . MO of diazirine correlates with the LUMO of the carbene, and the LUMO of the three-membered ring with the HOMO of the carbene. The crossing of the MO's occurs at TR. However, if the motion of the  $\text{C}_3$  fragment during the dissociation reduces the molecular symmetry to  $C_s$ , then the HOMO of diazirine correlates directly with the HOMO of the carbene. There is a corresponding correlation of the LUMO's. Consequently this pathway is symmetry allowed. Exactly this mechanism is underlying the thermal dissociation which passes through the transition state  $\text{TS}_0$  according to our calculations.

**5.3. 3-Formyldiazirine.** We present the potential surfaces of the reaction of 3-formyldiazirine to 2-diazoacetaldehyde in Figure 9. They were optimized with the same accuracy as the previous cases. There is a strikingly complicated structure of the excited hypersurfaces above the ground state of the three-membered ring.

(43) J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **97**, 5217 (1975).

(44) H. F. Schaefer III, *Acc. Chem. Res.*, **12**, 288 (1979).

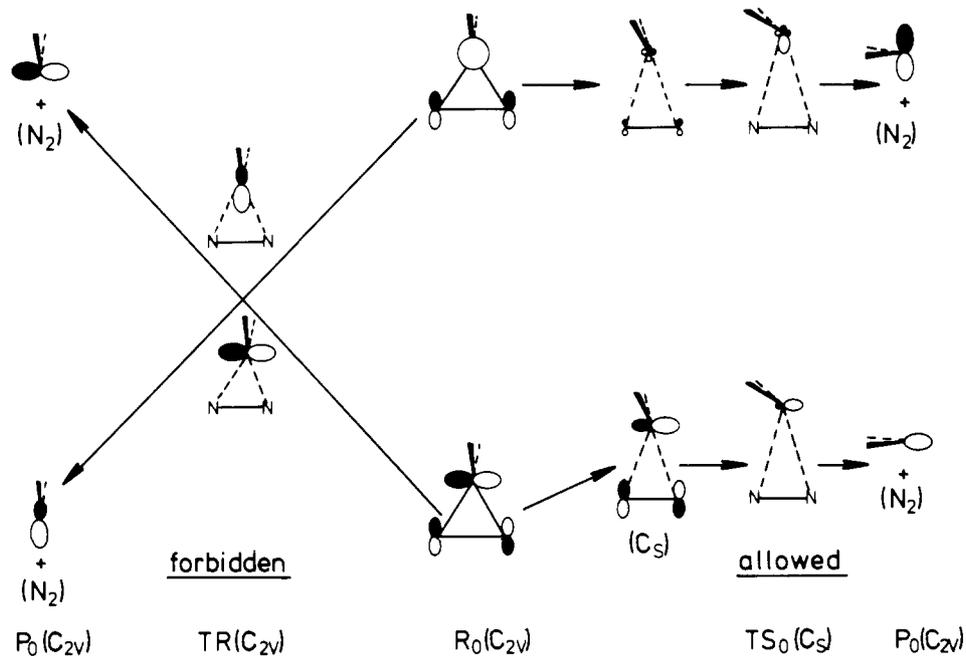


Figure 8. MO correlation diagram for the symmetry-allowed and forbidden thermal dissociation of 3,3-dimethyldiazirine.

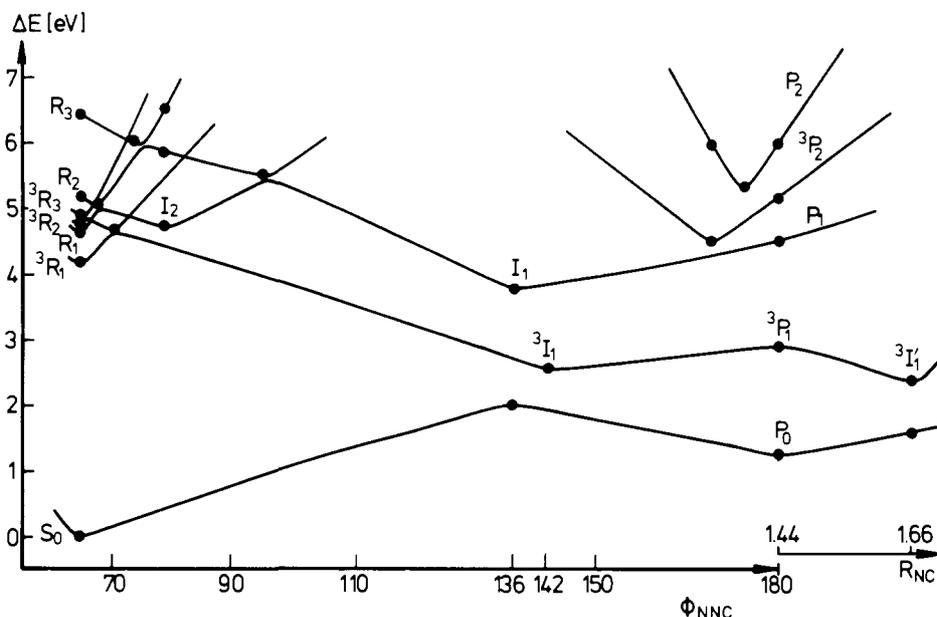


Figure 9. Potential curves for the photochemical isomerization of 3-formyldiazirine to 2-diazoacetaldehyde: ●, points of optimized geometry.

An excitation into the  $R_3(^1n_N\sigma^*)$  state will lead first to a symmetrical ring opening in analogy to the previously investigated diazirines. During this process there is an avoided crossing with the  $R_1$  surface. Here the symmetry of  $R_3$  is reduced to  $C_1$ . At an angle  $\phi_{\text{NNC}} = 73^\circ$ , both surfaces have minimal energy separation. If a radiationless transition occurs at this point, a part of the molecules will be allowed to move to the  $R_1$  minimum. The rest will be confronted with a second avoided crossing at  $\phi_{\text{NNC}} = 95^\circ$  with further ring opening. Here the original  $R_2$  state hinders spontaneous isomerization. From this point both the  $R_2$  minimum  $I_2$  and the intermediate  $I_1$  at  $\phi_{\text{NNC}} = 136^\circ$  can be reached. The radiationless transition from the  $I_1$  minimum to the  $R_0$  surface can lead to ground state of the linear or of the cyclic molecule, as well as to the dissociated product  $\text{N}_2 + \text{carbene}$  with the additional energy.

If the excitation occurs in the first absorption region of 3-formyldiazirine, both the  $R_1$  and the  $R_2$  state can be occupied. From the second singlet, radiationless transitions may lead to the  $R_1$  minimum under conservation of  $C_s$  symmetry. If the symmetry is reduced by a distortion of the ring, the  $I_2$  minimum can be

reached in part through the region of an avoided crossing between  $R_1$  and  $R_2$ . From  $R_1$  a barrier of 0.5 eV leads to  $I_2$ . From there an additional 0.65 eV is necessary to make isomerization possible.

From the two lower lying singlet states, additional transitions to the triplet surfaces  $^3R_1$ ,  $^3R_2$ , and  $^3R_3$  are possible. If the  $C_s$  symmetry is retained here after the ISC process, then the  $^3R_1$  state is finally populated. However, through distortion of the ring some molecules will reach the triplet intermediate  $^3I_1$  at an angle  $\phi_{\text{NNC}} = 142^\circ$  via avoided crossings and the thereby enforced internal conversion.

From our investigations we may conclude that electronically excited 3-formyldiazirine returns primarily by fluorescence or phosphorescence to the ground state. Only a small percentage of the excited molecules will form 2-diazoacetaldehyde. The behavior of the linear molecules in their excited states is more clearly describable as we see from the right part of Figure 9. After an excitation from  $P_0$  to  $P_1$ , the  $I_1$  minimum can be reached spontaneously under ring closure. The  $P_2$  and  $^3P_2$  surfaces show pronounced minima. The  $^3P_1$  state appears as transition state for the dissociation from the  $^3I_1$  intermediate. Another minimum  $^3I_1$

appears at dissociation with a NC distance of 1.66 Å.

The following conclusion is now possible. The rearrangement of 2-diazoacetaldehyde to 3-formyldiazirine should occur photochemically more easily than the retro reaction. This agrees with the experimental results on the system 3-diazo-2-oxoindoline/2'-oxospiro[diazirine-3,3'-indoline].<sup>13</sup> However, contrary to these results we find the thermal isomerization also favored from the linear to the cyclic compound.

## 6. Summary and Outlook

In this work we have clarified the photochemical reaction mechanisms of the molecules diazirine, 3,3-dimethyldiazirine, and 3-formyldiazirine. It can be shown that the step which primarily leads to the reaction stems from the excitation to a  $^1n\sigma^*$  state.  $^1n\pi^*$  states will be relevant only after further thermal excitation via internal conversion. Nonnegligible intersystem crossing to repulsive  $^3n\sigma^*$  surfaces can also lead to reaction.

In agreement with experiment our investigations show that methylene and dimethylcarbene (or propene) appear as the main products of photolysis of diazirine and 3,3-dimethyldiazirine. Diazomethane can appear as a by-product. We further determine that an equilibrium will be formed in the system 3-formyl-

diazirine/2-diazoacetaldehyde which should be both photochemically and thermally on the side of the ring if the linear molecule does not dissociate irreversibly. Diradicals and zwitterions are not found in the three reactions studied.

For the synchronous thermal reaction of 3,3-dimethyldiazirine we determine a symmetry-allowed pathway. We may generalize that such symmetry allowed mechanisms should occur in symmetrically substituted diazirines.  $\alpha$ -Ketodiazirines should be particularly prone to isomerization.

For a full clarification of photochemical reaction mechanisms of diazirines, other molecules with different substituent groups should be theoretically investigated. Among them are spiro compounds of the type of pentamethylenediazirine as well as  $\alpha$ -diazoamides and halogen-substituted diazirines.

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**Registry No.** Diazirine, 157-22-2; 3,3-dimethyldiazirine, 5161-49-9; 3-formyldiazirine, 98875-86-6; diazomethane, 334-88-3; 2-diazopropane, 2684-60-8; dimethylcarbene, 40852-89-9; 2-diazoacetaldehyde, 6832-13-9.

# MNDO and ab Initio Study of the Reduction of Formaldehyde by Lithium Methylamide

Michael L. McKee

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849.  
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**Abstract:** Theoretical methods were used to study the reduction of formaldehyde to methanol by lithium methylamide ( $\text{LiNHCH}_3$ ) as a model for the reduction of ketones to alcohols by lithium dialkylamides. The proposed mechanism involves the formation of a reactant complex composed of a dimer model ( $\text{LiNH}_2\text{:LiNHCH}_3$ ) coordinated to formaldehyde through one lithium. A hydrogen  $\beta$  to nitrogen is transferred to the carbon of formaldehyde, forming methoxide which is stabilized by lithium complexation. The reactant complex is predicted to be in a potential minimum 14.1 kcal/mol deep with respect to the complex  $\text{LiNH}_2\text{:LiNHCH}_3$  plus  $\text{H}_2\text{C=O}$  while the transition structure is 30.6 kcal/mol higher than the reactant complex. The thermodynamic driving force for the lithium-mediated reduction is the formation of the product complex which is 28.8 kcal/mol more stable than the reactant complex. A transition structure was found for nucleophilic addition of the methoxide ion to the  $\text{C=N}$  bond of the product complex, which would form aminomethoxymethane upon hydrolysis. However, the product complex is favored thermodynamically, and little condensation product is expected under equilibrium conditions. An alternative mechanism was considered in which the reactant complex consisted of the lithium methylamide monomer (rather than dimer) complexed to formaldehyde. The hydride transfer then occurs through a distorted six-membered cyclic transition structure. From a comparison of the two mechanisms, the effect of aggregation is discussed. All predictions refer to the gas phase.

The first report of the reduction of benzophenone by lithium dialkylamides was made by Wittig<sup>1</sup> in 1962. The reaction was originally concluded to proceed via a concerted  $\beta$ -hydride transfer from the base to the ketone. A single electron-transfer mechanism has more recently been proposed<sup>2</sup> based on the observation of various coupling products. It now appears<sup>3</sup> that the original interpretation was correct and that the products from radical precursors are formed from secondary reactions. The following study was undertaken to determine the energetics of a concerted

hydride shift mechanism in the gas phase.

## Method

Calculations were carried out at the restricted Hartree-Fock level by using MNDO<sup>4</sup> and the GAUSSIAN 82 program series.<sup>5</sup> Full optimizations using a multiparameter search routine<sup>6</sup> were carried out for all geometries

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