and products are determined by the combined effect of the mass action laws and diffusion. The fluctuations are defined as the instantaneous deviation of the number density at any point r from the uniform average value given by eq 5, e.g.

$$\delta\rho_{\mathrm{A}}(r,t) = \rho_{\mathrm{A}}(r,t) - \bar{\rho}_{\mathrm{A}} \qquad \text{(A-1)}$$

$$\delta\rho_{\mathrm{A}_2}(r,t) = \rho_{\mathrm{A}_2}(r,t) - \bar{\rho}_{\mathrm{A}_2}$$

The relevance of these fluctuations for diffusion-controlled[5-8] reactions is that their spatial correlation functions are related to the radial distribution function and, thereby, to the bimolecular rate constant (cf, eq 4). For the dimerization reaction at steady state, the precise relationship is[6]

$$g_{\mathrm{AA}}(|r - r'|) = 1 - \delta(r - r')/\rho_{\mathrm{A}}^{\mathrm{ss}} + \langle \delta\rho_{\mathrm{A}}(r,t)\, \delta\rho_{\mathrm{A}}(r',t)\rangle^{\mathrm{ss}}/\rho_{\mathrm{A}}^{\mathrm{ss}2} \qquad \text{(A-2)}$$

where $\langle \cdots \rangle$ represents the ensemble average. At steady state, the fluctuations for the dimerization reaction in eq 3 are Gaussian random variables satisfying the coupled stochastic differential equations;[5-8,12]

$$\partial\delta\rho_{\mathrm{A}}/\partial t = -4k^{\mathrm{obs}}\rho_{\mathrm{A}}^{\mathrm{ss}}\delta\rho_{\mathrm{A}} + 2k\delta\rho_{\mathrm{A}_2} + D_{\mathrm{A}}\nabla^2\delta\rho_{\mathrm{A}} + \tilde{f}_{\mathrm{A}} \qquad \text{(A-3)}$$

$$\partial\delta\rho_{\mathrm{A}_2}/\partial t = 2k^{\mathrm{obs}}\rho_{\mathrm{A}}^{\mathrm{ss}}\delta\rho_{\mathrm{A}} - k\delta\rho_{\mathrm{A}_2} + D_{\mathrm{A}_2}\nabla^2\delta\rho_{\mathrm{A}_2} + \tilde{f}_{\mathrm{A}_2}$$

The terms $\tilde{f}_{\mathrm{A}}$ and $\tilde{f}_{\mathrm{A}_2}$ are purely random Gaussian contributions to the time rates of change that vanish on the average and have the following space–time correlation functions:

$$\langle \tilde{f}_{\mathrm{A}}(r,t)\, \tilde{f}_{\mathrm{A}}(r',t') \rangle = (4k^{\mathrm{obs}}\rho_{\mathrm{A}}^{\mathrm{ss}2} + 4k\rho_{\mathrm{A}_2}^{\mathrm{ss}} - 2D_{\mathrm{A}}\rho_{\mathrm{A}}^{\mathrm{ss}}\nabla_r^{\,2})\, \delta(r-r')\, \delta(t-t') \qquad \text{(A-4)}$$

$$\langle \tilde{f}_{\mathrm{A}_2}(r,t)\, \tilde{f}_{\mathrm{A}}(r',t') \rangle = \langle \tilde{f}_{\mathrm{A}}(r,t)\, \tilde{f}_{\mathrm{A}_2}(r',t') \rangle = -2(k^{\mathrm{obs}}\rho_{\mathrm{A}}^{\mathrm{ss}2} + k\rho_{\mathrm{A}_2}^{\mathrm{ss}})\, \delta(r-r')\, \delta(t-t')$$

$$\langle \tilde{f}_{\mathrm{A}_2}(r,t)\, \tilde{f}_{\mathrm{A}_2}(r',t') \rangle = (k^{\mathrm{obs}}\rho_{\mathrm{A}}^{\mathrm{ss}2} + k\rho_{\mathrm{A}_2}^{\mathrm{ss}} - 2D_{\mathrm{A}_2}\rho_{\mathrm{A}_2}^{\mathrm{ss}}\nabla_r^{\,2})\, \delta(r-r')\, \delta(t-t')$$

By using Fourier transforms,[6] eqs A-3 and A-4 can be solved for the steady-state density–density correlation function on the right-hand side of eq A-2. This yields the radial distribution function exhibited in eq 7.

Theoretical Study of Several Diazaalkenes and Diazaalkyl Radicals

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Abstract: The stabilities of different isomers of several diazaalkenes (diazapropene, diazabutene, and diazapentene) were compared at several levels of theory. For the simplest diazaalkenes, methyldiazene (1,2-diaza-1-propene) and formaldehyde hydrazone (2,3-diaza-1-propene), the two isomers are very close in energy. At the MP4/6-311+G**//MP2/6-31G* level including zero-point and heat capacity corrections, the 1,2-isomer is 0.4 kcal/mol more stable than the 2,3-isomer. Bond dissociation energies were calculated for the formation of the diazapropenyl radical and the diazabutenyl radical. The best calculated BDE for the C—H bond in $HN{=}NCH_3$ (1,2-diaza-1-propene) is 87.3 kcal/mol while the N—H bond in $H_2NN{=}CH_2$ (2,3-diaza-1-propene) has a BDE value of 86.9 kcal/mol. The lowest energy diazabutene isomer is the hydrazone isomer, 1,2-diaza-2-butene, which is 2.4 kcal/mol more stable than the two azo isomers.

Introduction

The 1,2-diazapropene/2,3-diazapropene (azo/hydrazone) tautomeric pair is similar to the keto–enol system in that shifting a hydrogen in the hydrazone/azo system shifts the double bond from N═N to N═C while in the keto–enol system the double bond shifts from C═O to C═C. However, the azo/hydrazone system has received much less attention both theoretically and experimentally. In the liquid phase, the hydrazone 5,6-diaza-4-decene ($C_4H_9NHN{=}CHC_3H_7$) has been found[1] to be 3.3 kcal/mol more stable than the azoalkene 5,6-diaza-5-decene ($C_4H_9N{=}NC_4H_9$). By comparison, the keto form of acetone has an enthalpy 13.9 kcal/mol lower than its enol form in the gas phase.[2] The present study is undertaken to determine which form (azo/hydrazone) is more stable in the gas phase and to understand the factors leading to that preference. By determining the bond dissociation energy (BDE) for loss of the most weakly bound hydrogen, the radical stabilizing ability of the -N═NR group can be determined.

Previous theoretical calculations on formaldehyde hydrazone include a MNDO study[3] of the *E–Z* isomerization of **2**, an ab initio study[4] on conformations and *E–Z* isomerizations of **2** and **7** at the MP2/6-31G**//4-31G and HF/6-31G**//4-31G levels, respectively, an ab initio study[5] of **2** and protonated **2** at the HF/6-31G** level, and a recent study[6] of **2** and the radical cation

Table I. Compound Number, Name, and Formula List of Species Studied

no.	name	formula
1	1,2-diaza-1-propene	$HN{=}NCH_3$
2	2,3-diaza-1-propene	$H_2NN{=}CH_2$
3	diazapropenyl radical	$HNNCH_2$
4	2,3-diaza-2-butene	$CH_3N{=}NCH_3$
5	2,3-diaza-1-butene	$H_2C{=}NNHCH_3$
6	1,2-diaza-1-butene	$HN{=}NCH_2CH_3$
7	1,2-diaza-2-butene	$H_2NN{=}CHCH_3$
8	1,2-diazabutenyl radical	$HNNCHCH_3$
9	2,3-diazabutenyl radical	H_2CNNCH_3
10	2,3-diaza-2-pentene	$CH_3CH_2N{=}NCH_3$
11	3,4-diaza-2-pentene	$CH_3CH{=}NNHCH_3$

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Table II. Calculated Energy Separation between the Azo (**1**, **4**, **6**, **10**) and Hydrazone (**2**, **5**, **7**, **11**) Isomers[a] ($R_2N{=}NCH_2R_1$ and $R_2HNN{=}CHR_1$)

	$R_1{=}R_2{=}H$ **1/2**	$R_1{=}H$; $R_2{=}CH_3$ **4/5**	$R_1{=}CH_3$; $R_2{=}H$ **6/7**	$R_1{=}R_2{=}CH_3$ **10/11**
//6-31G*				
HF/6-31G*	2.1	5.8	-2.1	-0.2
PMP2/6-31G*	0.0	4.6	-4.0	-1.2
PMP4/6-31G*	1.2	5.6	-2.6	0.1
+ZPC/C_p	1.5	6.0[b]	-2.4[b]	(0.7)[c]
//6-31G**				
HF/6-31G**	0.3			
PMP2/6-31G**	-1.2			
PMP4/6-31G**	0.0			
+ZPC/C_p	0.3			
HF/6-311+G**	-0.2			
PMP2/6-311+G**	-1.6			
PMP4/6-311+G**	-0.2			
+ZPC/C_p	0.1			
//MP2/6-31G*				
HF/6-311+G**	-1.9			
PMP2/6-311+G**	-1.3			
PMP4/6-311+G**	0.1			
+ZPC/C_p[d]	0.4			
exptl				3.3[e]

[a] A positive number indicates that the azo form is more stable than the hydrazone. [b] The relative energies for **4**–**7** are 2.4, 8.4, 2.4, and 0.0 kcal/mol, respectively. [c] The zero-point and heat capacity corrections are estimated. [d] Zero-point and heat capacity corrections are made at the HF/6-31G** level. [e] For the liquid phase $R_1 = C_3H_7$ and $R_2 = C_4H_9$.

Table III. Comparison of Geometric Parameters and Dipole Moment in the Diazapropenyl Radical, 1,2-Diazapropene, and 2,3-Diazapropene

	HF/6-31G* //6-31G*	HF/6-31G** //6-31G**	MP2/6-31G* //MP2/6-31G*
	Diazapropenyl Radical (**3a**)		
NN	1.316 (65%)[a]	1.316 (66%)[a]	1.333 (57%)[a]
NC	1.316 (32%)[a]	1.316 (32%)[a]	1.294 (6%)[a]
NNC	112.7°	112.8°	111.6°
dipole moment	0.64	0.67[b]	0.69[b]
	1,2-Diazapropene (**1**)		
N=N	1.214	1.214	1.264
NC	1.453	1.453	1.464
NNC	113.6°	113.6°	111.2°
dipole moment	0.51	0.57[b]	0.60[b]
	2,3-Diazapropene (**2**)		
NN	1.371	1.368	1.385
N=C	1.251	1.251	1.284
NNC	118.4°	118.5°	116.7°
dipole moment	2.18	2.18[b]	2.28[b]

[a] Elongation expressed as a percentage of the double to single bond increase of the same bond in **1** and **2**. [b] The dipole moments are calculated with the 6-311+G** basis set.

Table IV. Relative Energies of Radical at //6-31G** Geometries

	HF/ 6-31G**	PMP2/ 6-31G**	PMP4/ 6-31G**	corrected
$HNN{=}CH_2$ $^2A''$ **3a**	0.0	0.0	0.0	0.0
$HNN{=}CH_2$ $^2A'$ **3b**	23.1	17.4	18.7	18.2
$HNN{=}CH_2$ $^2A''$ **3c**	31.3	18.0	19.7	18.6
$HNN{=}CH_2$ $^2A'$ **3d**	31.2	14.2	16.4	15.3
$HNN{=}CH_2$ ^2A **3e**	11.4	8,6	7.7	7.3
$NHNCH_2$ ^2A **3f**	18.6	11.0	12.7	13.7

Table V. Calculated N–H and C–H Bond Dissociation Energies (kcal/mol)

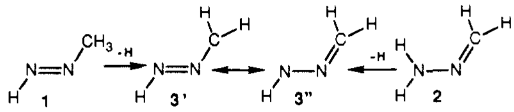
	$R_1 =$ $R_2 = H$		$R_1 = H$; $R_2 = CH_3$		$R_1 = CH_3$; $R_2 = H$	
	C–H (**1**)	N–H (**2**)	C–H (**4**)	N–H (**5**)	C–H (**6**)	N–H (**7**)
//6-31G*						
HF/6-31G*	66.1	64.0	64.2	58.4	59.3	61.4
PMP2/6-32G*	85.3	85.3	85.6	81.1	80.2	84.2
PMP4/6-31G*	86.4	85.2	85.0	79.4	80.1	82.8
+ZPC/C_p[a]	79.2	77.7	77.6	71.4	72.1	75.3
//6-31G**						
HF/6-31G**	65.1	64.8				
PMP2/6-31G**	89.2	90.4				
PMP4/6-31G**	90.5	90.5				
+ZPC/C_p	81.7	84.0				
HF/6-311+G**	84.3	64.0				
PMP2/6-311+G**	63.8	92.5				
PMP4/6-311+G**	90.9	91.3				
+ZPC/C_p	84.9	84.8				
//MP2/6-31G*						
HF/6-311+G**	61.1	62.9				
PMP2/6-311+G**	92.8	94.1				
PMP4/6-311+G**	93.5	93.4				
+ZPC/C_p[b,c]	87.3	86.9				

[a] At this level of theory the BDE of CH_4 is 96.5 kcal/mol. [b] At this level of theory the BDE of CH_4 is 100.7 kcal/mol. [c] Zero-point and heat capacity corrections are at the HF/6-31G** level.

of **2** at the HF/6-31G* level. High-level calculations have been reported by Tomašić and Scuseria[7] for the energy difference between methyldiazene (**1**) and formaldehyde hydrazone (**2**). In this study[7] a triple-ζ basis set augmented by two sets of polarization functions on all atoms and a set of f-functions on non-hydrogens was used in conjunction with the CCSD electron correlation treatment to predict an energy separation of 2,0 kcal/mol in favor of **2**. The authors report that the second set of polarization functions increases the stability of the hydrazone relative to the diazene by 0,9 kcal/mol.

Method

All calculations employ the GAUSSIAN 86 program system.[8] Geometries of the parent tautomeric pair (**1**, **2**) and allylic-type radical resulting from H loss (**3**) have been optimized at the HF/6-31G*, HF/6-31G**,



and MP2/6-31G* levels (UHF and UMP2 for radicals), and single-point calculations were done at the MP4 level of electron correlation with the

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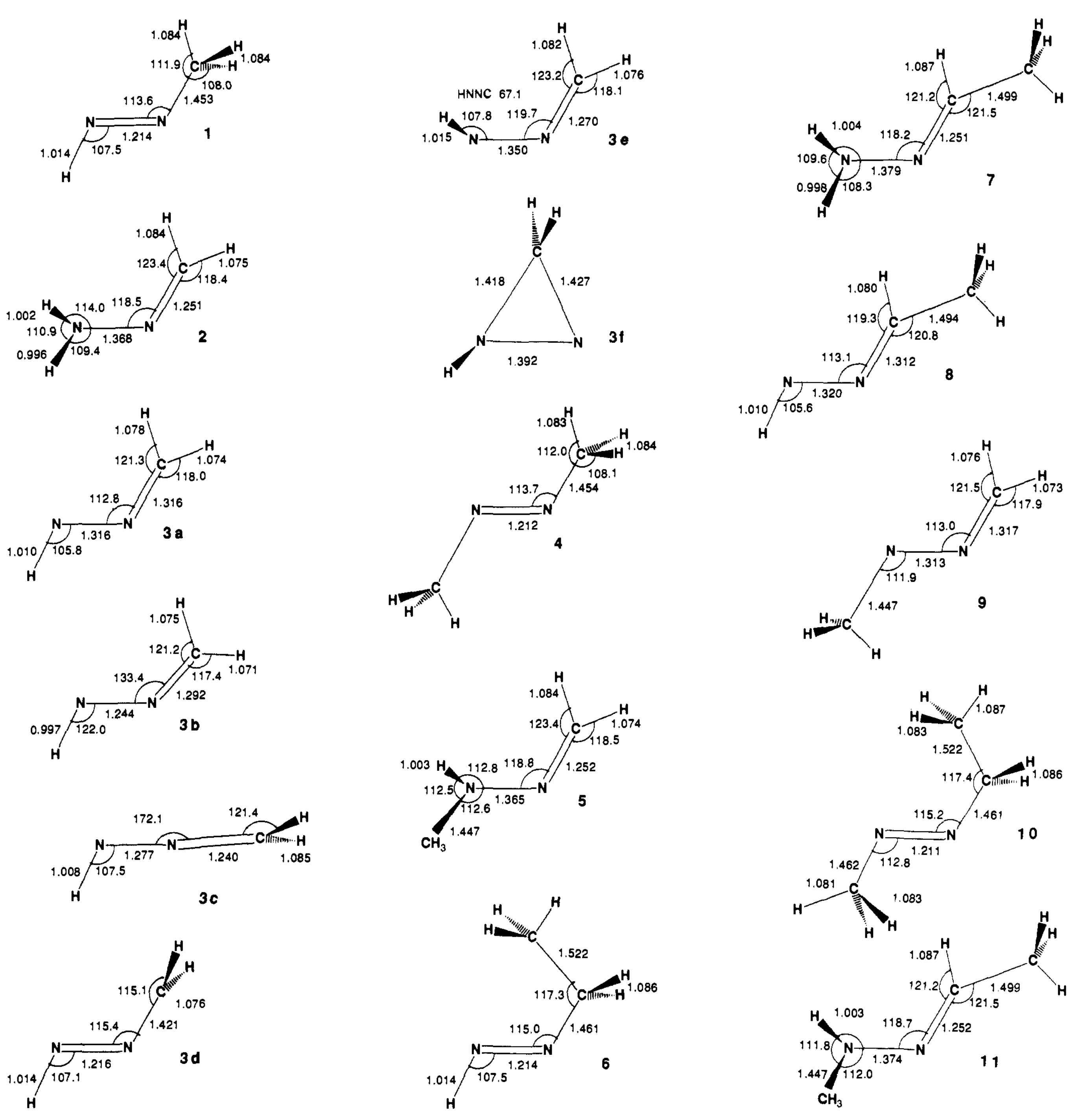

Figure 1. Selected geometric parameters are given at the HF/6-31G** level for structures **1**-**3** and at the HF/6-31G* level for structures **4**-**11**. In all cases only the lowest energy conformation is indicated. Values at the HF/6-31G* and MP2/6-31G* levels for structures **1**-**3** may be found in Table III.

6-31G*, 6-31G**, and 6-311+G** basis sets. Larger systems were optimized only at the HF/6-31G* level, and single-point calculations were made at the MP4/6-31G* level.[9] The effect of spin contamination has been projected out of the MP energies by the spin-projection method developed by Schlegel and co-workers.[10] Zero-point corrections have been weighted by a 0.9 factor,[9] and heat capacity corrections have been made at 298 K. All electron correlation calculations were done in the frozen-core approximation. A notation, name, and formula list is given in Table I, and selected geometric parameters are given in Figure 1 and Table II for the structures studied. Absolute energies, zero-point energies, and projected spin-squared values are available as supplementary material; relative energies are given in Tables III-V.

Results and Discussion

The relative energy of **1** and **2** (Table II) is relevant to synthetic chemists since reactions involving the formation of an azo compound often suffer from the simultaneous formation of an unwanted hydrazone.[11] At all levels the energies of **1** and **2** are within 2.1 kcal/mol. At the corrected MP4/6-31G*//6-31G* level, **1** is 1.2 kcal/mol lower than **2** (1.5 kcal/mol with zero-point and heat capacity corrections). Higher levels of theory stabilize **2** relative to **1**, and at the highest level **1** is more stable than **2** by only 0.4 kcal/mol.

The 1,2-diazapropenyl radical **3a** is formed from methyldiazene **1** or formaldehyde hydrazone **2** by removal of a hydrogen on carbon or nitrogen, respectively. The radical is isoelectronic with

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[9] For a description of basis sets and the 0.9 weighting factor for frequencies see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[10] Sosa, C.; Schlegel, *Int. J. Quantum Chem.* **1986**, *29*, 1001. Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

[11] March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 533.

the allyl radical and should be stabilized by the resonance structures 3′ and 3″.[12] The geometries of 3 calculated at various levels are compared in Table III. The contributions of 3′ and 3″ were assessed by calculating the percent elongation of the N–N or N–C bond in the radical compared to a localized double bond in **1** or **2** where the NN or NC bond should be localized as a single or double bond in the two isomers. Equation 1 gives the percent elongation of the N–N bond where a small percentage would

$$\frac{\mathrm{N{-}N_{radical}} - \mathrm{N{=}N_{azo}}}{\mathrm{N{-}N_{hydrazone}} - \mathrm{N{=}N_{azo}}} \times 100 = \%\ \text{elongation} \qquad (1)$$

indicate a localized double bond and a large percentage would indicate a localized single bond. An analogous equation can be written for the percent elongation of the N–C bond. At all levels the NC bond appears to have more double bond character; at the MP2/6-31G* level the NC bond is only elongated by 6% relative to the hydrazone **2**. Hence, the resonance structure 3″ appears to dominate, a conclusion also consistent with bond energies.[13]

The rotation of either terminal group of the diazapropyl radical is another probe into the relative importance of the two resonance structures, 3′ and 3″. In agreement with the analysis of structural parameters above, the rotational barrier (**3a** → **3d** (TS) → **3a**) about the C-N bond (15.3 kcal/mol, Table IV) is significantly higher than the rotational barrier (**3a** → **3e** (TS) → **3a**) about the N-N bond (7.3 kcal/mol). For comparison, the measured rotational barrier for the methylene group in the allyl radical is slightly greater than 15 kcal/mol.[14]

The planar σ radical **3b** (^{2}A′) is predicted to be less stable than the π radical **3a** (^{2}A″) because the unpaired σ electron cannot interact with the π electrons. Calculations confirm this and find the σ radical **3b** to be 18.2 kcal/mol less stable than **3a**. The inplane repulsion of the unpaired electron opens the NNC angle of **3b** by 20.6° compared to **3a**, and the absence of π interaction reduces the N=C bond in **3b** by 0.024 Å. It should be pointed out that the barrier for methylene rotation is computed as the difference between the ^{2}A″ state (**3a**) and the ^{2}A′ state (**3d**) since, as the methylene group rotates, the orbital containing the unpaired electron also rotates from a position perpendicular to the molecular plane (^{2}A″ state) to a position in the molecular plane (^{2}A′ state). An analysis of the rotated ^{2}A″ state (**3c**) indicates that it represents the transition state for inversion at nitrogen. For comparison the 3-membered-ring **3f** was also computed; it lies 13.7 kcal/mol above the planar ^{2}A″ state (Table IV).

Bond Dissociation Energies. Bond dissociation energies (BDE) were calculated for **1** → **3a** and **2** → **3a** as well as for the methyl-substituted diazaalkenes **4**–**7** (Table V). The SCF theory gives BDE's for **1** and **2** over 20 kcal/mol lower than the correlation calculations. Including electron correlation, zero-point corrections and heat capacity effects, the bond dissocation energies for C–H (**1**) and N–H (**2**) are 79.2 and 77.7 kcal/mol, respectively (MP4/6-31G*//6-31G* + ZPC/C_p). Polarization functions on hydrogens increase the BDE of C–H and N–H by 2.5 and 6.3 kcal/mol, respectively (MP4/6-31G**//6-31G** + ZPC/C_p). Enlarging the basis set to 6-311+G** (triple-ζ + diffuse + polarization) increases the BDE by 3.2 and 0.8 kcal/mol, respectively (MP4/6-311+G**//6-31G** + ZPC/C_p). Finally, optimizing geometries at the MP2/6-31G* level increases the BDE by another 2.4 and 2.1 kcal/mol for the C–H and N–H BDE to yield a "best value" of 87.3 and 86.9 kcal/mol, respectively. If we can assume that BDE of methyl-substituted systems will behave similarly, geometry and basis set effects will increase the BDE calculated at the MP4/6-31G*//6-31G* + ZPC/C_p level by 8–9 kcal/mol.

Replacing a hydrogen on nitrogen in **1** or **2** with a methyl group to give **4** or **5**, respectively, decreases the C–H BDE by 1.6 kcal/mol and the N–H BDE by 6.3 kcal/mol. On the other hand, replacing a hydrogen on carbon in **1** or **2** with a methyl group to give **6** or **7**, respectively, decreases the C–H BDE by 7.1 kcal/mol and the N–H BDE by 2.4 kcal/mol.

Radical Stabilization Energies. Radical stabilization energy[15] (RSE) is a measure of a substituent's ability to stabilize a methyl radical relative to hydrogen and is useful for determining which substituents might best be used for stabilizing a radical center. The RSE of the α-azomethyl radical (HN=N) is calculated according to eq 2 and compared with experimental RSE for HC=O, H_2C=CH, and NH_2.

$$\mathrm{X\text{-}CH_3 + CH_3 \rightarrow X\text{-}CH_2 + CH_4} \qquad (2)$$

$$\text{RSE (kcal/mol)} = 13.4\ (\mathrm{X = HN{=}N}),$$
$$13^{16}\ (\mathrm{X = HC{=}O}),\ 19^{17}\ (\mathrm{X = H_2C{=}CH}),\ 19^{18}\ (\mathrm{X = NH_2})$$

These values are simply the difference between the BDE value of the C–H bond in **1** and the C–H BDE in CH_4. They should be more reliable than the calculated BDE since there should be some cancellation of error in the relative BDE values. The calculated C–H BDE in CH_4 is underestimated by 4.4 kcal/mol at the MP4/6-311+G**//MP2/6-31G* + ZPE/C_p level (105.1, exptl;[20] 100.7 kcal/mol, calc). It is probable that the error in the BDE of **1** is in the same direction. At this level the calculated RSE of the α-azomethyl group is 13.4 kcal/mol, which can be compared to the experimental RSE of a HC=O group of 13 kcal/mol.[16] The O–CH–CH_2 radical is isoelectronic with HN–N–CH_2 and is characterized by two resonance structures analogous to 3′ and 3″. It is therefore reasonable that the RSE would also be similar.[12] The RSE for the vinyl group is larger, which indicates that the allyl radical (CH_2–CH–CH_2) is stabilized to a larger extent due to equal contribution of the two resonance structures. Thus, the α-azomethyl group should not be as effective as a vinyl or amino group in stabilizing an alkyl radical but should be comparable to an acyl group.

Energetics. Replacing a hydrogen on carbon of **1** or **2** with a methyl group (to give species **6** and **7**) increases the stability of the hydrazone form **7** relative to the azo form **6** (Table II). At the MP4/6-31G*//6-31G* + corrections level 1,2-diaza-2-butene (**7**) is 2.4 kcal/mol more stable than 1,2-diaza-1-butene (**6**). The effect of higher level calculations on **1** and **2** suggests that the difference would increase by about 1 kcal/mol. If the methyl group replaces a hydrogen on nitrogen rather than on carbon (to give species **4** and **5**) the azo form **4** is 6.0 kcal/mol more stable than the hydrazone form **5**. Thus, when the nitrogens are in the 1 and 2 positions, the hydrazone form is more stable, and when the nitrogens are in the 2 and 3 positions, the azo form is more stable.

When a methyl group replaces a hydrogen on both nitrogen and carbon to give **10** and **11**, the azo form **11** is favored by 0.1 kcal/mol at the MP4/6-31G* level. If ZPC and C_p corrections are estimated from the monomethylated isomers, the azo form is favored by 0.7 kcal/mol. Lastly, if the effects of improving geometry and basis sets are assumed to be the same in the dimethylated isomer as for **1** and **2**, then the hydrazone will be stabilized an additional 1.1 kcal/mol. Thus, the lowest energy form switches and the hydrazone form **11** is predicted to be about 0.3 kcal/mol more stable than the azo form **10** in the gas phase.

Experimentally, ΔH_f of $C_4H_9NHN{=}CHC_3H_7$ is 3.3 kcal/mol smaller than ΔH_f of $C_4H_9N{=}NC_4H_9$ in the liquid phase,[1] which should be very similar to the difference between **11** and **12**. While

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an error of 3 kcal/mol at this level of theory is certainly possible, a reasonable argument can be put forth that the two isomers should be closer in energy in the gas phase than in the liquid phase. The dipole moment of **11** ($CH_3CH{=}NNHCH_3$) is calculated to be 1.95 D compared to a value of 0.05 D for **10** ($CH_3N{=}NCH_2CH_3$). Therefore, internal hydrogen bonding in the hydrazone form should be larger than in the azo form (the azo form also has no hydrogens suitable for hydrogen bonding), which would lead to a greater heat of vaporization for the hydrazone. Thus, while the hydrazone form is 3.3 kcal/mol more stable than the azo form in the liquid phase, in the gas phase the difference in the heats of formation would be reduced by the difference in the heats of vaporization.

Conclusion

The azo radical has more N-C double bond character than N-N double bond character as demonstrated by a calculation of structural parameters and the N-C and N-N rotational barriers. Addition of a hydrogen to the radical at either the carbon or nitrogen terminus produces either the azo form or the hydrazone form with nearly equal exothermicity. Substitution of a methyl for a hydrogen on carbon increases the stability of the hydrazone form while the substitution of a methyl for a hydrogen on the terminus nitrogen increases the stability of the azo form.

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Supplementary Material Available: Tables of absolute energies in hartrees (4 pages). Ordering information is given on any current masthead page.

Abnormally Narrow C-M-C Angle in $M(L_1)L_2$ Complexes (M = Si, Al, Mg, Na; L_1 and L_2 = CO, CN)

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Abstract: The geometries and the binding energies of AlCO and $Al(CO)_2$ were calculated by the ab initio molecular orbital methods. The geometry of AlCO is linear, and the calculated Al-C bond distance depends on the electron correlation effects, The bond angle C-Al-C in $Al(CO)_2$ is 70-74°, and the binding energy between the Al atom and CO is four or five times larger than that (2-4 kcal/mol) of AlCO. In AlCO, the electron repulsion between the n orbital of CO and the 3s orbital of the Al atom is essential. Important for $Al(CO)_2$ are the 3s → 3p polarization on Al induced by the delocalization from the n orbitals of two CO's to the 3p orbital (a_1 symmetry) of Al. The electronic reorganization involves the cyclic $\overline{\text{n–3s–3p–n}}$ orbital interaction that is controlled by the orbital phase continuity-discontinuity properties. The geometries of $M(L_1)L_2$ complexes for various electronic states of four main metal atoms were also calculated by the ab initio MO methods. M is silicon, aluminum, magnesium, and sodium atoms, and L_1 and L_2 are CO or CN molecules. From the calculated results, the C-M-C angle decreases with increasing occupation number for the metal state, which is an index for the electronic configuration of the metal and decreases with decreasing electronegativity of the metal atom.

1. Introduction

The interactions of small molecules with metal atoms, clusters, and surfaces have been extensively studied both experimentally and theoretically.[1-3] One of the recent focuses is the structure of $Al_x(CO)_y$ complexes. Matrix isolation spectroscopy has provided particularly valuable data. The products of condensation of Al and CO have been studied by IR[2] and ESR[3] methods. These studies showed that $Al(CO)_2$ is the major product. No evidence for the formation of AlCO was obtained. From the IR intensities of the symmetric and asymmetric CO stretching modes the C-Al-C angle was predicted to be about 110° on the assumption that the Al-C-O bonds are linear.

On the other hand, the AlCO and $Al(CO)_2$ complexes have been reported in a few theoretical papers.[4-6] These studies showed that the AlCO complex has small binding energy. In the $Al(CO)_2$ complex, the C-Al-C angle was predicted at about 70°.[5,6] Recently, Grev and Schaefer[7] reported the structure of $Si(CO)_2$ by the SCF MO and CI methods. The C-Si-C angle was estimated at about 78-80°. However, the abnormally narrow bond angles have not been interpreted in a convincing manner.

Table I. Geometry Parameters and Binding Energies of the AlCO Complex

optimization method	geometry, Å		binding energy, kcal/mol, 6-31G(d)			
	Al-C	C-O	HF	MP2	MP3	MP4-(SDTQ)
HF/3-21G	3.486	1.127	−0.79	−2.15	−1.82	−2.09
HF/6-31G(d)	3.740	1.113	−0.87	−1.85	−1.60	−1.79
MP2/3-21G	2.289	1.177	5.55	−3.97	−2.42	−3.89
MP2/6-31G(d)	2.128	1.165	6.33	−4.70	−3.32	−4.41

In this paper we first present the results of ab initio MO calculations on AlCO and $Al(CO)_2$ and propose that the geo-

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