Electronic States of Aminonitrene (1,1-Diazine). A Study of the Endwise Bonding of Dinitrogen[1a]

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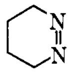
Abstract: The ground and excited states of aminonitrene (1,1-diazine), H_2NN, were studied using generalized valence bond (GVB) and configuration interaction (GVB-CI) wave functions. We find that the ground state is a singlet state ($^1A_1$) with the triplet ($^3A_2$) lying 15 kcal/mol higher. (In the Hartree–Fock description, the triplet state is 5 kcal *below* the singlet, indicating the necessity of including electron-correlation effects.) The stabilization of the singlet state is due to a large amount of double bond character in the NN bond ($H_2N^+{=}N{:}^-$) as reflected in the short bond length (R_e = 1.25 Å) and the large dipole moment (μ = 4.036 D). In contrast, the $^3A_2$ state has R_e = 1.37 Å and μ = 2.35 D. With extensive CI we find an NN bond energy of $D_0(H_2NN)$ = 69 kcal/mol, leading to a heat formation of $\Delta H_{f_{298K}}(H_2NN)$ = 90 kcal/mol. The character of higher excited states and ions is also discussed. Some predictions of the thermochemistry of 1,1-diazines are provided.

I. Introduction

A number of chemically interesting systems incorporating molecular dinitrogen bonded to an organic or inorganic framework are currently under extensive investigation by various groups.

Using transition metals it has been possible to bond N_2 to a single metal complex[2] M-N-N and to incorporate N_2 bridging two metal complexes[3] M-N-N-M. From such complexes it has been possible to reduce the N_2 to hydrazine (N_2H_4) or ammonia (NH_3) by reaction with hydrogen.[2,3]

An exciting area of organic dinitrogen systems has been with ring systems such as the 1,2- and 1,1-diazines, where the extrusion of nitrogen may lead either to formation of biradical intermediates or to concerted eliminations.[4]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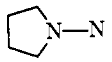
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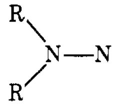
Of particular theoretical interest are the electronic structure and bond energies of aminonitrenes such as in **2** since these systems are poorly understood. It is generally presumed[5] that the ground state of **3** is a singlet state as would be expected from the valence bond diagram (1). However, nitrenes R-N generally have a triplet ground state, with the first singlet state much higher (44 kcal/mol for NH). Previous ab initio theoretical studies of aminonitrene resulted in a *triplet ground state* with the singlet state higher by 26.3,[6] 31.5,[7] 2.08,[8] and 5.2 kcal/mol,[9] respectively.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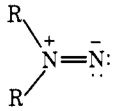
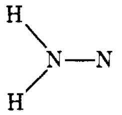

(1)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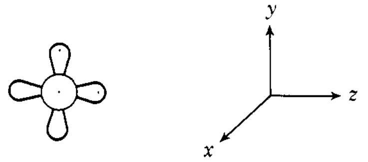
In this paper we will concentrate on aminonitrene, **4**. We carried out Hartree-Fock (HF), generalized valence bond[10] (GVB), and configuration interaction (GVB-CI) calculations on both the singlet and triplet states with geometry optimization. From these studies we find that the HF wave function leads to the triplet state 5.3 kcal below the single but that electron-correlation effects reverse the ordering leading to a singlet ground state with the triplet 15 kcal/mol higher.

In addition we obtained bond energies and dipole moments of these states and examined several other excited states and cation states for the optimum ground state geometry.

First (section II) we will summarize the quantitative results while presenting a qualitative description of the states of **4**. This is followed by section III presenting the details of the calculations and section IV discussing the orbitals. Section V provides other results including a discussion of the thermochemistry of various 1,1-diazines.

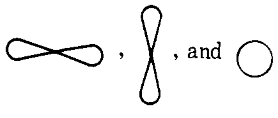
II. Qualitative Description and Summary of Results

A. Atomic States. The ground state of N is ^4S and has the configuration $(1s)^2(2s)^2(2p)^2$. Ignoring the 1s and 2s pairs we can represent this wave function as

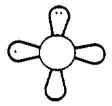


(2)

where



represent p_z, p_y, and p_x orbitals, respectively, and each dot indicates one electron in the orbital. With three electrons in the p orbitals we can also construct the ^2D and ^2S states lying at 2.4 and 3.6 eV above the ^4S state.[11] Configurations such as (3) must lead to a doublet state; the single configuration (3) is half ^2D and half ^2P.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B. Simple Nitrenes. Bonding an H to (2) leads to (4) where the line indicates a singlet bonding pair. Triplet pairing of the p_x and p_y orbitals of (4), as in (2), leads to the $^3\Sigma^-$ ground state of NH. Other couplings and occupations of the p_x and p_y or-

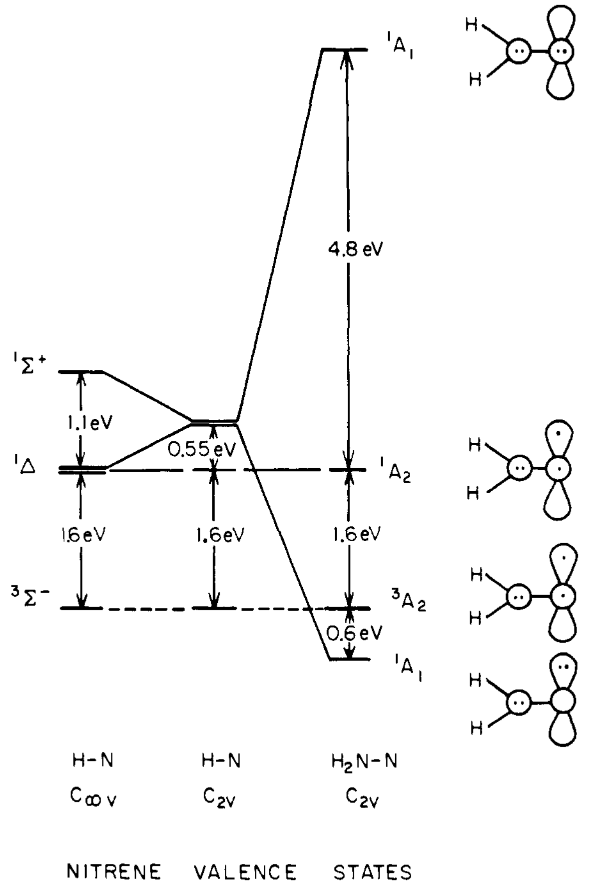
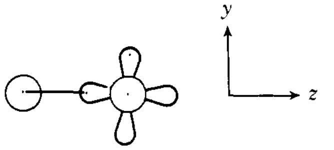


Figure 1. Energies of the valence states of nitrene (HN, from ref 12) and aminonitrene (H_2NN).



(4)

bitals lead to the $^1\Delta$ and $^1\Sigma^+$ states of NH lying[12] at 1.6 and 2.7 eV above $^3\Sigma^-$. The wave functions for these states have the form

$$^3\Sigma^-: (p_xp_y - p_yp_x)(\alpha\beta + \beta\alpha) \quad (5a)$$

$$^1\Delta^-: (p_xp_y + p_yp_x)(\alpha\beta - \beta\alpha) \quad (5b)$$

$$^1\Delta^+: (p_xp_x - p_yp_y)(\alpha\beta - \beta\alpha) \quad (5c)$$

$$^1\Sigma^+: (p_xp_x + p_yp_y)(\alpha\beta - \beta\alpha) \quad (5d)$$

where we have ignored the bond pairs and closed-shell orbitals which should be similar for the various states. In this description

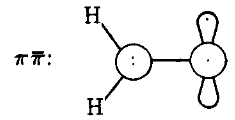
$$E(^1\Delta) = E(^3\Sigma^-) + 2K_{xy} \quad (6a)$$

$$E(^1\Sigma^+) = E(^3\Sigma^-) + 4K_{xy} \quad (6b)$$

where K_{xy} is the usual two-electron exchange integral. Since K_{xy} is necessarily positive, the states increase in energy with the sequence $^3\Sigma^-$, $^1\Delta_1$, and $^1\Sigma^+$. The $^3\Sigma^-$-$^1\Delta$ and $^1\Delta$-$^1\Sigma^+$ separations, 1.6 and 1.1 eV, respectively, are not quite equal, indicating the approximate character of this simple description.[13] Simple alkyl nitrenes, RN, such as CH_3N (**5**), should lead to a very similar bonding description.

C. Aminonitrene, $\pi\bar{\pi}$. We can now consider the effect of replacing the H group of nitrene, HN, with an amino group to give aminonitrene **4**. Joining an amino radical ($^2A_1$) with (2), to form a planar molecule **4** leads to (7) where the σ bond

$\pi\bar{\pi}$:

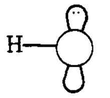


(7)

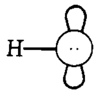
is represented as a line and only the three nonbonded orbitals are indicated explicitly. This configuration (7) is referred to as $\pi\bar{\pi}$, indicating that there is one electron in the π orbital and one electron in the $\bar{\pi}$ orbital. (An orbital that is symmetric with respect to the molecular plane but antisymmetric with respect to the perpendicular plane passing through the CC axis is denoted by $\bar{\pi}$.) Triplet and singlet pairing of the singly occupied orbitals of (7) leads to the $^3A_2(\pi\bar{\pi})$ and $^1A_2(\pi\bar{\pi})$ states of **4** analogous to the $^3\Sigma^-$ and $^1\Delta^-$ states of NH, (5a) and (5b), respectively. The main difference between the $\pi\bar{\pi}$ states in aminonitrene and in nitrene is the presence of the π lone pair on the amino nitrogen; however, the interaction of this pair with the nitrene π orbital should be equivalent in both the $^1A_2(\pi\bar{\pi})$ and $^3A_2(\pi\bar{\pi})$ states. Therefore we would expect the $^1A_2$-$^3A_2$ separation in aminonitrene to be ~1.6 eV, just as in NH.

The results of our calculations are illustrated in Figure 1. As can be seen the $^1A_2$-$^3A_2$ separation is 1.6 eV in agreement with these simple predictions.

D. Aminonitrene, $\bar{\pi}^2$. We now want to determine the effect of the amino lone pair on the $^1\Delta^+$ and $^1\Sigma^+$ states of nitrene. Each of these states is a combination of two configurations, (8)

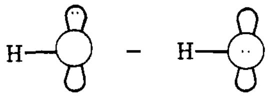


(8)

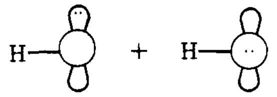


(9)

and (9). In nitrene, these two configurations are equivalent and can mix to a resonant combination ($^1\Delta^+$) (10) and to an antiresonance combination ($^1\Sigma^+$) (11). In aminonitrene configurations (8) and (9) become (12) and (13). Here we find

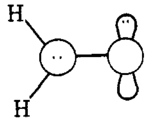


(10)



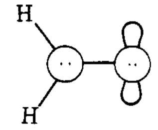
(11)

$\bar{\pi}^2$:



(12)

π^2:



(13)

great differences due to the effect of the π pair of the NH_2 group. In (12) this pair can delocalize into the empty π orbital of the terminal N whereas in (13) there are two doubly occupied π orbitals and hence very repulsive interactions (arising from the Pauli principle). This interaction with the NH_2 group splits the states (12) and (13) by ~7 eV. Since this effect is far greater than the favorable interaction due to the resonance observed in (10) and (11) for NH, we expect no significant interaction between (12) and (13).

Ignoring the interaction with the NH_2 group, the configurations (12) and (13) would be expected to lie about 2.2 eV above the $^3A_2(\pi\bar{\pi})$ state in analogy to NH; see Figure 1. In fact

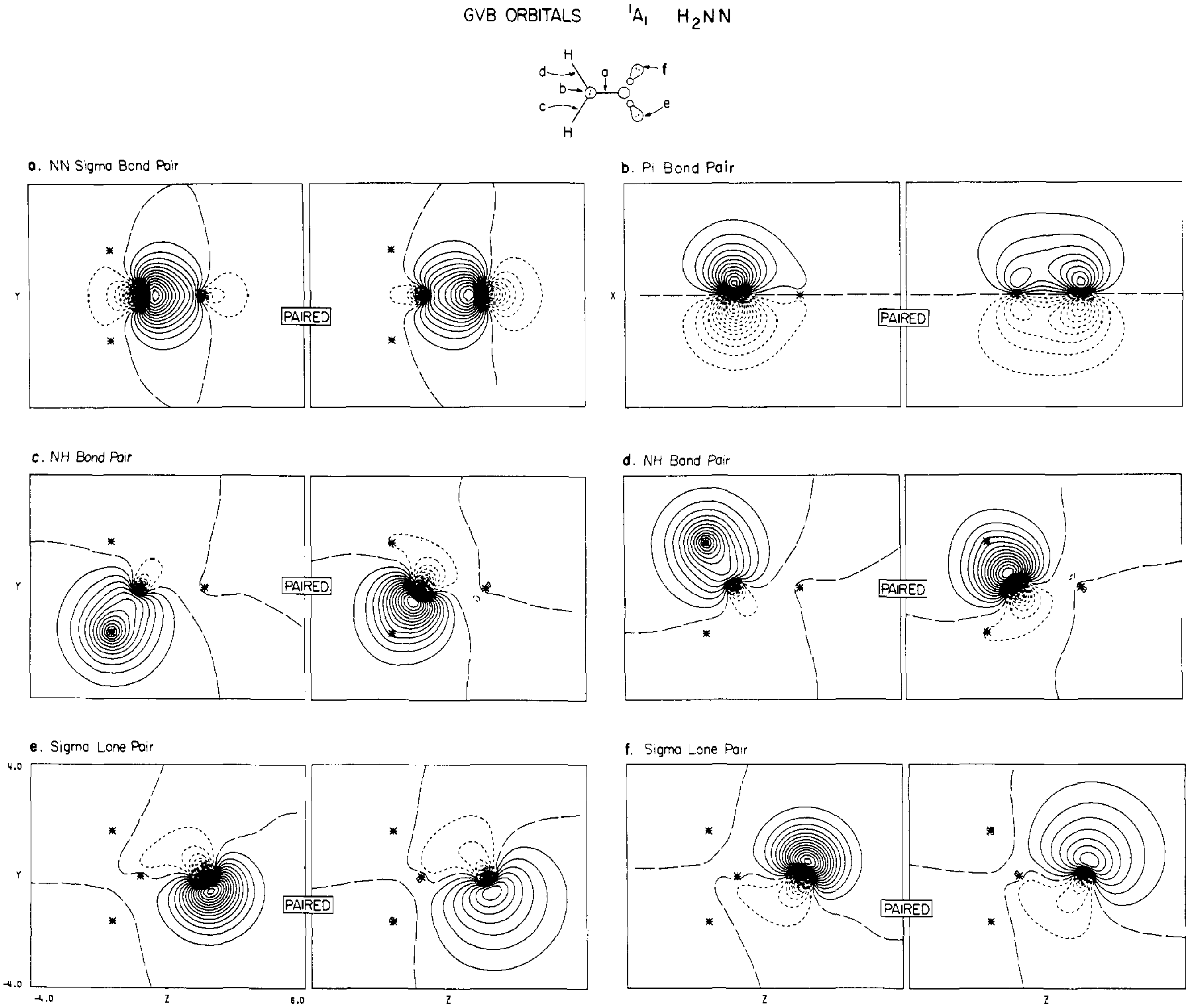
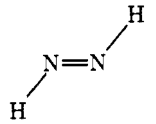


Figure 2. GVB orbitals of the $^1A_1$ state of aminonitrene based on the GVB(6/15) wave function. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au. The same conventions are used for all plots.

we find that $^1A_1(\bar{\pi}^2)$ is 0.6 eV *below* $^3A_2(\pi\bar{\pi})$, indicating about 2.8 eV of bonding in the π orbitals of (12). Indeed the π system of $^1A_1(\bar{\pi}^2)$ is quite delocalized, strongly resembling the π orbitals of a normal π bond, as shown in Figure 2. Similarly, the calculated NN bond length of 1.25 Å for the $^1A_1$ ($\bar{\pi}^2$) state of H_2NN is equal to the value[14] 1.25_2 Å observed for diimide **6**.



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This indicates that the bond order for $^1A_1$ aminonitrene is two. In addition, the dipole moment for the $^1A_1$ state is 4.0 D (negative on nitrene end) indicating that dipolar species such as (1) contribute heavily.

The calculated location of $^1A_1(\pi^2)$ indicates about 4.2 eV of repulsive interaction due to the two π pairs.

E. Nonplanar Geometries. So far we have considered the states of aminonitrene assuming a planar geometry. The π^2 configuration (13) is expected to adopt a pyramidal geometry to reduce the overlap (and thus the repulsion) of the two doubly occupied orbitals. Similarly, configuration (12) would undoubtedly prefer a planar configuration to maximize the π bonding.

On the other hand, the optimum geometry for configuration (7) is not so obvious from such qualitative considerations. Here there are two opposing forces: (1) a pyramidal geometry would reduce the antibonding interaction of the singly occupied π orbital with the doubly occupied amino π group (Pauli principle); (2) a planar geometry could allow delocalization of the amino π pair onto the nitrene nitrogen, leading to a three-electron, two-center bond. Our calculations indicate that these effects are comparable. The optimum geometry is pyramidal; however, the inversion barrier is <1 kcal/mol. (For comparison, the inversion barrier of NH_3 is 6 kcal.[15]) The delocalization is clear in the shape of the π orbitals, Figure 3, and is reflected in the optimum bond length (R_{NN} = 1.37 Å) for the $^3A_2$ state. While this bond is longer than the 1.25 Å of the $^1A_1$ (π) state, it is considerably shorter than the typical single NN bond length (e.g., 1.45 Å in hydrazine[16]). This delocalization is also reflected in the dipole moment, which is calculated to be 2.35 D.

III. Calculational Details

A. Basis Set and Geometries. The Dunning[17] (3s2p/2s) contraction of the Huzinaga (9s5p/4s) primitive Gaussian basis was used in all calculations. We also included one set of d-polarization functions (α = 0.8) for each nitrogen. Such functions are important in calculating the singlet-triplet energy

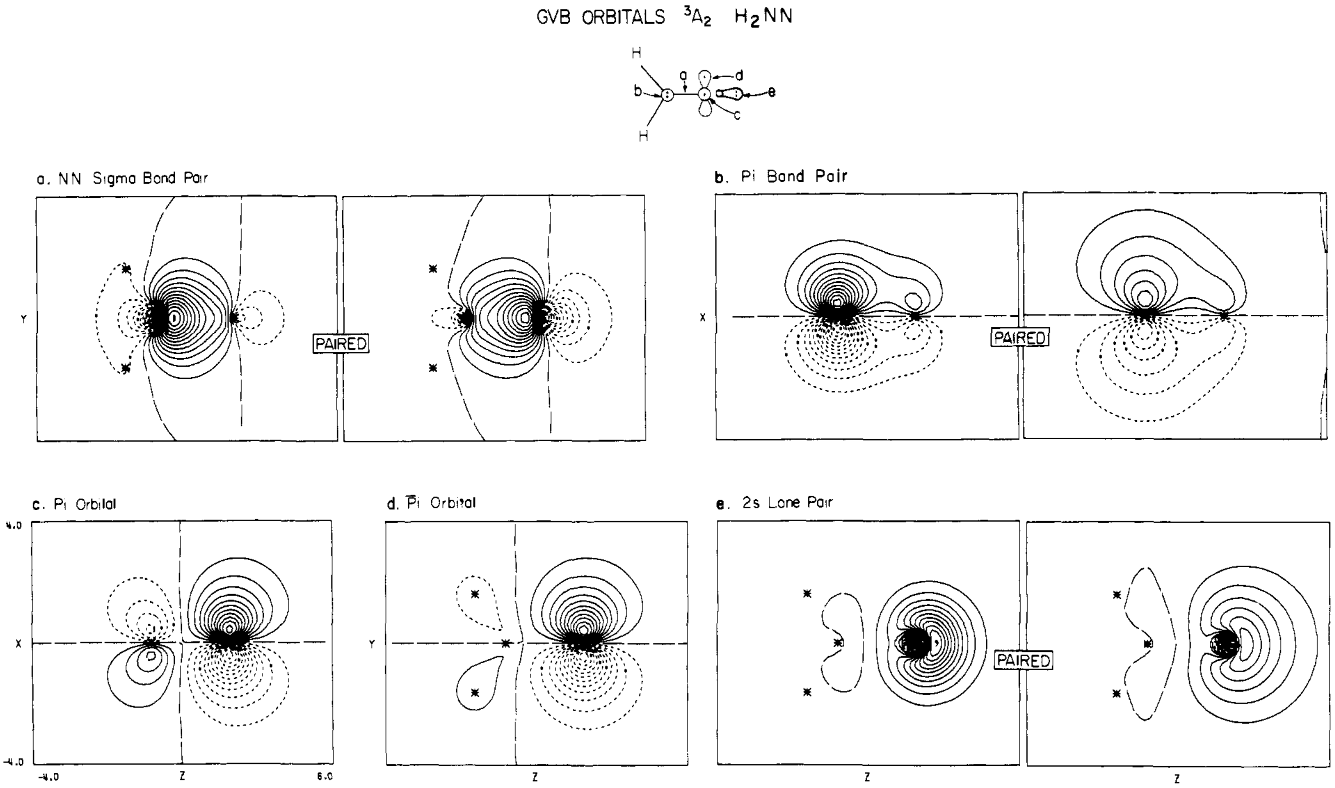


Figure 3. Selected GVB orbitals of the $^3A_2$ state of aminonitrene based on GVB(6/15) wave function.

difference for methylene[18] and thus should also be important in nitrene, an analogous system.

In the planar states, we considered only geometries with C_{2v} symmetry and used the following parameters: $R_{\text{N-H}} = 1.016$ Å; ∠HNH = 115.4°.[19] Since the most likely difference in geometry between the $\pi\bar{\pi}$ and $\bar{\pi}^2$ states was expected to be in the nitrogen-nitrogen bond length, this parameter was optimized (a cubic spline fit to four points: $R_{\text{N-H}} = 1.23$, 1.33, 1.43, and 1.53 Å). The $^1A_1$ state was found to have an optimum bond length of 1.24_6 Å, while the $^3A_2$ state has a bond length of 1.37_4 Å. These optimum values were used in all subsequent calculations.

To determine the optimum pyramidal geometry for the lowest triplet state, the N-H and N-N bond lengths were fixed at 1.016 and 1.374 Å, while the HNH and NNH bond angles were varied linearly.

We compared the geometries from HF minimal basis set calculations on N_2H_4, H_2N_2, and NH_3 by Pople and coworkers[7] with experimental values of N_2H_4 and NH_3[16] and estimated that pyramidal triplet H_2N_2 would have ∠HNH = 107.0° and ∠NNH = 119.0°, while planar H_2N_2 $^3A_2(\pi\bar{\pi}^2)$ would have ∠HNH = 115.4° and ∠NNH = 122.3°. Extrapolating linearly we included a third point ∠HNH = 102.1° and ∠NNH = 117.1°. Letting θ be the angle between the NN axis and the H_2N plane, these points correspond to $\theta = 0$, 35.4, and 43.7°. Since $dE/d\theta = 0$ at $\theta = 0$, the above three calculations correspond to five points, which we fitted with cubic splines to obtain the optimum geometry. This crude geometry search provides only semiquantitative data on the optimum pyramidal angle and inversion barrier but is sufficient for our purposes here.

B. The GVB Calculations. The HF wave function for the $^1A_1$ state of aminonitrene has eight doubly occupied orbitals. Breaking the nitrogen-nitrogen bond while retaining the planar geometry yields the $^2A_1$ amino radical and ^2P nitrogen atom and hence requires HF wave functions consisting of seven doubly occupied orbitals and two singly occupied orbitals. Thus an HF wave function does not properly describe the dissociation of the NN bond. Indeed, as discussed in section I, the HF wave function leads to the wrong ground state for H_2NN, putting $^3A_2(\pi\bar{\pi})$ below $^1A_1(\bar{\pi}^2)$.

The GVB wave function allows every electron to have its own orbital. However, to describe properly the dissociation of the NN bond of the $^3A_2(\pi\bar{\pi})$ state, it is sufficient that only one HF pair be correlated or split into pairs of nonorthogonal singly occupied orbitals. This pair corresponds to the NN σ bond, which is directly involved in bond breaking. This wave function, in which only the NN σ bond is correlated, is denoted as GVB(2) [or GVB(2/4)], since there are two pairs of electrons that are not closed-shell.

For the $^1A_1(\bar{\pi}^2)$ state the wave function consistent with the GVB(2) wave function for $^3A_2(\pi\bar{\pi})$ is the GVB(2) wave function in which both the NN σ bond and the $\bar{\pi}$ lone pair are correlated. However, near R_e we expected (and found) that the amino lone pair exhibits delocalization characteristic of a π bond pair, and hence we also correlated this pair. For large R the most important correlation for the amino lone pair will be in-out correlation in which one electron occupies a more contracted orbital while the other occupies a more diffuse orbital. Near R_e the most important correlation is left-right (between the two nitrogens). A consistent description should allow both correlations, requiring three natural orbitals for this π pair. Since the NN σ bond pair and the π lone pair are each described by two natural orbitals, the resulting wave function has three electron pairs that are not closed-shell (doubly occupied) and these three pairs are described with a total of seven natural orbitals; thus this wave function is denoted GVB(3/7) or more simply as GVB(3).

In order for the $^3A_2$ wave function to be consistent with that of the $^1A_1(\bar{\pi}^2)$ state, we also correlated the amino π pair of $^3A_2$. Thus we solved for the GVB(3) wave function of $^3A_2(\pi\bar{\pi})$.

Although the above wave functions are expected to be adequate for geometry optimization, accurate excitation energies and bond strengths require close attention to small correlation effects not included in these wave functions.

To obtain an accurate NN bond energy requires correlation

Table I. Pair Quantities for the GVB(6/15) Calculations[b]

State	Energy	Pair	Overlap	Energy lowering
$^1A_1$	−110.08267	NN σ[a]	0.872	0.0181
		NH left	0.840	0.0172
		NH right	0.840	0.0172
		π bond[a]	0.712	0.0293
		$\bar{\pi}$ lone pair	0.876	0.0095
		2s lone pair	0.876	0.0095
$^3A_2$	−110.05526	NN σ[a]	0.831	0.0233
		NH left	0.844	0.0162
		NH right	0.844	0.0162
		π lone pair[a]	0.882	0.0083
		2s lone pair	0.919	0.0048
$^3A''$ (pyramidal, $\theta = 43.7°$)	−110.06442	NN σ[a]	0.827	0.0237
		NH left	0.840	0.0167
		NH right	0.840	0.0167
		π lone pair[a]	0.881	0.0106
		2s lone pair	0.919	0.0081

[a] These pairs were correlated with more than two natural orbitals; only the dominant two are used for the overlap, but all are used for the energy lowering. [b] All energies in hartree atomic units (1 hartree = 627.5096 kcal/mol).

Table II. Excitation Energies and Dominant Configurations for Aminonitrene [GVB(6/15)-CI][d]

State	Excitation energy,[a] eV	Configuration															Energy lowering, hartree
		NH bonds				NN σ bond				π lone pair			Lone pair		2s lone pair		
		a_1	a_1^*	$\bar{b}_2$	$\bar{b}_2^*$	σ	σ^*	σ^*	$\bar{\pi}$	π	π^*	π^*	π	$\bar{\pi}$	σ	σ^*	
$^1A_1$	0.00[b,d]	2	0	2	0	2	0	0	0	2	0	0	0	2	2	0	
		2	0	2	0	2	0	0	0	0	2	0	0	2	2	0	0.0167
		2	0	2	0	1	1	0	0	1	1	0	0	2	2	0	0.0142
		2	0	2	0	0	2	0	0	2	0	0	0	2	2	0	0.0103
$^3A_2$	0.65	2	0	2	0	2	0	0	0	2	0	0	1	1	2	0	
		2	0	2	0	0	2	0	0	2	0	0	1	1	2	0	0.0155
		2	0	1	1	2	0	0	0	1	1	0	1	1	2	0	0.0078
		2	0	2	0	1	1	0	0	1	0	0	1	1	2	0	0.0074
$^1A_2$	2.22	2	0	2	0	2	0	0	0	2	0	0	1	1	2	0	
		2	0	2	0	2	0	0	0	1	0	0	2	1	2	0	0.0149
		2	0	2	0	0	2	0	0	2	0	0	1	1	2	0	0.0143
		2	0	2	0	1	1	0	0	1	0	0	2	1	2	0	0.0127
$^1A'$	7.08[c]	2	0	2	0	2	0	0	0	2	0	0	2	0	2	0	
		2	0	2	0	2	0	0	0	1	0	0	1	2	2	0	0.0071
		2	0	2	0	1	1	0	0	1	0	0	1	2	2	0	0.0019
		2	0	2	0	2	0	0	0	0	0	0	2	2	2	0	0.0013
$^3A_2$	8.84	2	0	2	0	2	0	0	0	1	0	0	2	1	2	0	
		2	0	2	0	1	1	0	0	1	0	0	2	1	2	0	0.0341
		2	0	2	0	1	1	0	0	2	0	0	1	1	2	0	0.0095
		2	0	2	0	0	1	0	0	1	0	0	2	1	2	0	0.0075
$^1A_2$	9.26	2	0	2	0	2	0	0	0	1	0	0	2	1	2	0	
		2	0	2	0	1	1	0	0	1	0	0	2	1	2	0	0.0355
		2	0	2	0	1	1	0	0	2	0	0	1	1	2	0	0.0096
		2	0	2	0	0	2	0	0	1	0	0	2	1	2	0	0.0080
$^1A_1$	13.29[b]	2	0	2	0	2	0	0	0	1	1	0	0	2	2	0	
		2	0	2	0	2	0	0	0	0	2	0	0	2	2	0	0.0234
		2	0	2	0	1	1	0	0	2	0	0	0	2	2	0	0.0200
		2	0	2	0	2	0	0	0	2	0	0	1	1	2	0	0.0139

[a] Planar triplet geometry unless specified. [b] Planar singlet geometry. [c] Pyramidal triplet geometry. [d] Total energy = −110.10915 hartrees. [d] The four dominant configurations for each state are listed.

of other pairs localized near the NN bond since there will be interpair correlation effects[20] important near R_e. Thus we increased the complexity of our GVB wave function by also correlating the orbitals corresponding to the two NH bonding pairs and the 2s nonbonding pair on the terminal nitrogen. This leads to GVB(6/13) wave functions for the $^3A_2$ and $^1A_1$ states. The GVB(6/13) wave function allows us to account for any differential correlation between the NH bond pairs of aminonitrene and those of amidogen (NH_2). From previous studies on ethylene,[21a] it was found that accurate bond strengths require the inclusion of two additional natural orbitals for the correlated CC σ bond. In analogy we have included this correlation in our NN bond leading to the GVB(6/15) wave function.

C. CI Calculations. Two different levels of CI wave functions were used. In determining the NN bond length, we carried out a full CI over the active orbitals of the GVB(3/7) wave function for $^1A_1$ and $^3A_2$. For the singlet this utilized all configurations of the GVB pairs and the nitrene lone pair (NN $\sigma\sigma^*$, $LP_1\pi\pi_1{}^*\pi_2{}^*$, $LP_2\bar{\pi}^2$) leading to 50 spatial configurations (104 determinants) of the proper spin and spatial symmetry. The analogous CI was performed for the triplet, resulting in 27 spatial configurations (65 determinants). Note here that by optimizing the orbitals of the GVB wave function we allow high orders of correlation in just a few configurations.

In determining the NN bond energy we carried out considerably more complicated CI calculations using the orbitals of the GVB(6/15) wave function. The reason is that it was

Table III. Ionization Potentials and Dominant Configurations for Aminonitrene [GVB(6/15)-CI][c]

State	Ionization potential,[a] eV	Configuration															Energy lowering, hartree
		NH Bonds				NN σ bond				π lone pair			Lone pair		2s lone pair		
		a_1	a_1*	b_2	b_2*	σ	σ*	σ*	$\bar{\pi}$	π	π*	π*	π	$\bar{\pi}$	σ	σ*	
$^2B_2$	9.40	2	0	2	0	2	0	0	0	2	0	0	0	1	2	0	
		2	0	2	0	2	0	0	0	1	0	0	1	1	2	0	0.0154
		2	0	2	0	1	1	0	0	1	0	0	1	1	2	0	0.0019
		2	0	2	0	2	0	0	0	0	0	0	2	1	2	0	0.0011
$^2B_1$	12.05	2	0	2	0	2	0	0	0	2	0	0	1	0	2	0	
		2	0	2	0	2	0	0	0	1	0	0	2	0	2	0	0.0359
		2	0	1	0	2	0	0	0	2	0	0	1	1	2	0	0.0139
		2	0	2	0	2	0	0	0	2	0	0	1	0	1	1	0.0121
$^4B_2$	12.27	2	0	2	0	2	0	0	0	1	0	0	1	1	2	0	
		2	0	2	0	0	2	0	0	1	0	0	1	1	2	0	0.0179
		2	0	1	1	2	0	0	0	1	0	0	1	1	2	0	0.0169
		2	0	2	0	2	0	0	0	0	1	0	1	1	2	0	0.0140
$^2B_2$	13.76	2	0	2	0	2	0	0	0	1	0	0	1	1	2	0	
		2	0	2	0	0	2	0	0	1	0	0	1	1	2	0	0.0173
		2	0	1	1	2	0	0	0	1	0	0	1	1	2	0	0.0162
		2	0	2	0	2	0	0	0	0	1	0	1	1	2	0	0.0132
$^2B_1$	13.86[b]	2	0	2	0	2	0	0	0	1	0	0	0	2	2	0	
		2	0	1	1	2	0	0	0	1	0	0	0	2	2	0	0.0138
		2	0	2	0	2	0	0	0	0	1	0	0	2	2	0	0.0120
		2	0	2	0	0	2	0	0	1	0	0	0	2	2	0	0.0111

[a] Planar triplet geometry unless specified. [b] Planar singlet geometry. [c] Energies are relative to the ground state ($^1A_1$) of the neutral. The dominant five configurations are listed for each state.

necessary to include a consistent level of correlation effects for both *N*-aminonitrene and the separated molecules (i.e., NH_2 and H).

(a) To account for all correlation effects involving the NN σ bond and π orbitals, we allowed up to quadruple excitations within the set of seven GVB orbitals ($\sigma\sigma_1{}^*\sigma_2{}^*\sigma_3{}^*\pi\pi_1{}^*\pi_2{}^*$) describing the four electrons of the NN σ bond and the π lone pair, with the restriction that there be no excitations between the σ and π sets. (In the $^3A_2$ case we also included in this CI the singly occupied π orbital on the terminal nitrogen.)

(b) In order to account for correlation effects available to the separated molecules but not normally utilized in aminonitrene and to include interpair correlation effects important in the molecule, we added another set of configurations involving all six pairs of GVB orbitals: A = NN($\sigma\sigma^*$); B = $LP_1(\pi\pi_1{}^*\pi_2{}^*)$; C = $NH_1(\sigma\sigma^*)$ + $NH_2(\sigma\sigma^*)$; D = 2s($\sigma\sigma^*$); and E = $LP_2(\bar{\pi},\bar{\pi}^*)$. Here we allowed all simultaneous double excitations within set A, within set B, and within set E simultaneous with all single excitations within set D and within set C but with the restrictions that (i) no excitations higher than quadruple be included and (ii) no excitations between sets be allowed.

(c) In addition to the above, all single excitations from the dominant configurations (three for $^3A_2$ and four for $^1A_1$) were included. The result of a, b, and c is 139 spatial configurations (256 spin eigenfunctions) of the proper symmetry for the $^1A_1$ case and 181 spatial configurations (687 spin eigenfunctions) of the proper symmetry for the $^3A_2$ case.

We should emphasize here that despite only a moderate number of configurations this wave function contains a very extensive level of correlation effects including a vast number of triple and quadruple excitations. This is possible since we have self-consistently determined the optimum correlating orbitals by carrying out the GVB calculations. This does two things for us. First, it reduces the number of orbitals that need be considered in the CI, greatly reducing the number of configurations resulting from a given level of CI. Second, since the GVB orbitals are localized with chemically identifiable character, we can develop conceptual schemes identifying which higher order correlations are essential. This serves the purpose of keeping down the total number of excitations (while including all important effects) but just as important, the conceptual scheme resulting from the GVB wave function allows us to compare wave functions of different states and geometries and thereby to establish (before calculations) consistent levels of correlation sufficient to trust excitation energies, bond energies, etc. Thus we have been able to benefit here from studies on ethylene and methylene[21] which established guidelines on consistent levels of correlation.

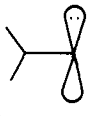
The configurations for the ion states (Table III) were generated just as for the $^1A_1$ and $^3A_2$ states using appropriate dominant configurations (see Table III). The orbitals and geometry were those from the $^3A_2$ state except as noted in Table III.

IV. The GVB Orbitals

A. The $^1A_1$ State. The GVB orbitals of the $^1A_1(\bar{\pi}^2)$ ground state are shown in Figure 2 [based on the GVB(6/12) wave function with only two natural orbitals in the NN σ bond pair and two in the NN π bond pair]. We find that the orbitals localize in different regions and have the basic character of valence bond wave functions.

In the σ system there are five different electron pairs. The first pair (A) corresponds to the NN σ bond; one orbital centered on the central nitrogen is hybridized[22] ($sp^{1.5}$) toward the terminal nitrogen, while the other orbital centered on the terminal nitrogen is hybridized ($sp^{5.0}$) toward the central nitrogen. The next two pairs (C, D) correspond to the NH σ bonds—one pair for each bond. The two pairs are identical and consist of two orbitals: one centered on the hydrogen is essentially spherical with some delocalization toward the central nitrogen, while the other is an sp^2-type orbital (actually $sp^{1.7}$) centered on the central nitrogen and hybridized toward the hydrogen.

In section II the description of the $^1A_1(\bar{\pi}^2)$ state involved a $\bar{\pi}$ lone pair (14) and a N 2s pair (15). However, with the



(14)

(15)

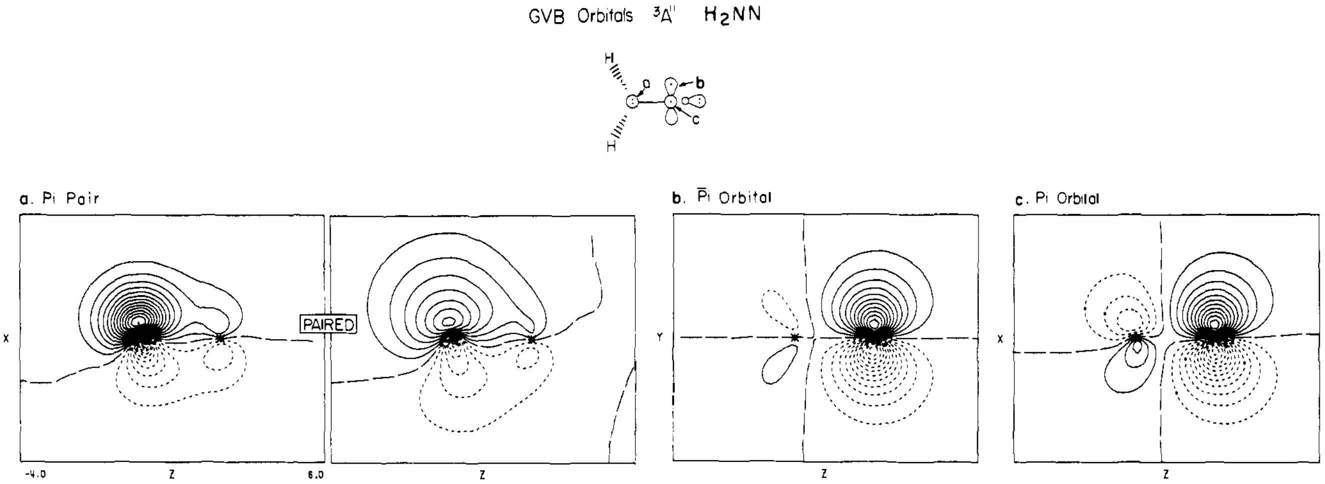
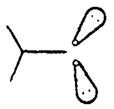


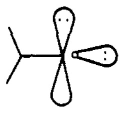
Figure 4. Selected GVB orbitals of the pyramidal (θ = 43.7°) $^3A''$ state of aminonitrene based on the GVB(6/15) wave function.

GVB(6) wave function we find that the orbitals (E, F) of Figure 2 have the form (16) [ignoring in (16) the correlation



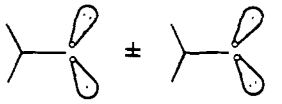
(16)

within each lone pair] where each lone pair has sp$^{1.3}$ hybridization. For a (closed-shell) HF wave function the energy of (16) and (17) would be identical (corresponding to combining



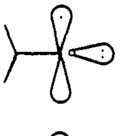
(17)

columns of the determinant wave function). However, for the GVB wave function, (16) and (17) lead to different energies with (16) being favored. The energy of the GVB(6) wave function of form (17) [contracted from the orbitals of the GVB(6) wave function for (16)] is 6 kcal higher than that of (16) so that the distinction between (16) and (17) is energetically of some importance. Exciting or ionizing one electron out of one of the lone pair orbitals leads to (18) based on (16)

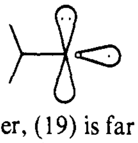


(18)

and (19a) or (19b) based on (17). Again these descriptions are



(19a)



(19b)

nearly equivalent; however, (19) is far simpler to represent and hence is preferred for discussing excited and cation states. Thus we continue to use (17) in describing $^1A_1(\bar{\pi}^2)$ although the orbitals can best be described as (16).

From Figure 2 we see that the π system [consisting of a doubly occupied lone pair orbital (B) on the central nitrogen] is considerably delocalized onto the terminal nitrogen, as expected from the earlier discussion (see section II).

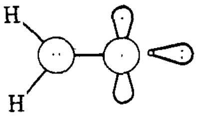
Energy lowerings and overlaps for these GVB orbitals are listed in Table I.

B. The $^3A_2$ State. The bonding pairs corresponding to the NH bonds (not shown) and NN σ bond (Figure 3a) are quite similar to the corresponding $^1A_1$ orbitals. (The new hybridizations are sp$^{2.2}$ for NH and sp$^{2.8}$ and sp$^{6.4}$ for the NN σ bond.)

The two triplet-coupled orbitals (π and $\bar{\pi}$) are essentially pure p_x and p_y orbitals centered on the terminal nitrogen (see Figure 3c,d). The π lone pair on the central nitrogen (Figure 3b) is delocalized somewhat onto the terminal nitrogen, with a corresponding amount of antibonding character in the singly occupied π orbital.

The remaining orbital on the nitrene N corresponds to a doubly occupied, N 2s-like orbital [hybridized (sp$^{0.15}$) along the z axis].

Thus the triplet state can best be represented as

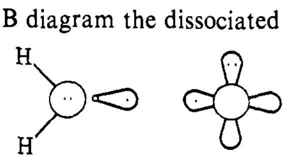


In Figure 4 we show the orbitals for the pyramidal $^3A''$ state (θ = 43.7°), resulting from bending hydrogens of the $^3A_2$ state out of the plane. The major change is that the delocalization of the π lone pair is reduced.

V. Additional Quantitative Results

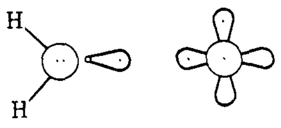
A. Heat of Formation. Since the GVB(6/15)-CI wave function for aminonitrene describes the correlation effects that change upon breaking of the nitrogen-nitrogen bond, we can expect accurate values for the bond dissociation energy of aminonitrene.

From the GVB diagram the dissociated $^1A_1$ state is (20)



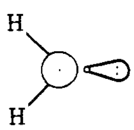
(20)

while the dissociated $^3A_2$ state is (21). Here we have retained



(21)

the planar geometry, forcing the NH$_2$ group to go to the $^2A_1$ excited state rather than the $^2B_1$ ground state (22). As dis-



(22)

cussed in section II, the configuration (3) for N in (20) describes neither ^2D nor ^2P [adiabatic dissociation of H$_2$NN ($^1A_1$) would lead to ^2D here].

Table IV. Contributions to the Dipole Moment of Aminonitrene[a] Based on the GVB(6/15) Wave Functions[b]

Orbitals	$^3A_2$ (planar, R_{NN} = 1.374 Å) y	z	$^1A_1$ (planar, R_{NN} = 1.246 Å) y	z
Non-GVB (1s)	0.0	0.0	0.0	−0.001
NH bonds				
Left	−0.360	−0.106	−0.354	−0.257
Right	0.360	−0.106	0.354	−0.257
2s pair	0.0	1.056	−1.429	0.454
$\bar{\pi}$	0.0	−0.126	1.432	0.442
NN σ bond	0.0	−0.029	−0.003	−0.091
π pair	0.0	0.548	0.0	1.297
π	0.0	−0.312		
Total σ	0.0	0.689	0.0	0.291
Total π	0.0	0.238	0.0	1.297
Total				
au	0.0	0.925	0.0	1.588
D	0.0	2.351	0.0	4.036

[a] A positive moment implies movement of electrons toward the nitrene end of the molecule. [b] All quantities in atomic units unless indicated otherwise; 1 au = 2.541765 D.

In order to obtain accurate bond energies we must carry out consistent calculations of both the molecule and the separate fragments. We elected to do this for the $^3A_2$ state and to calculate the bond energy of $^1A_1$ using the calculated excitation energy.

The basic principles in the CI calculations for bond energies are[21] (i) fully correlate (several natural orbitals) the bond pairs that are broken; (ii) correlate the orbitals for the other bond pairs and lone pairs associated with the atoms of the broken bond and allow single excitations in these pairs simultaneous with singles in the bond pairs (this allows the important interpair correlations that affect bond energies); (iii) in the case that either the molecule or separated fragment has empty valence orbitals or an open-shell configuration, include the appropriate strong mixing configurations. In some cases these principles will lead to a HF wave function of the dissociated fragment and in others to a correlated wave function.[23]

The relevant energies are given in Table V,[24] leading to a bond energy of $D_e'[H_2N\text{-}N(^3A_2)]$ = 89.2 kcal/mol for the planar $^3A_2$ state. In Table V we see that the HF wave function leads to an error of 43 kcal in the bond energy and that the perfect pairing GVB wave functions (without the additional interpair terms) lead to errors of 25–30 kcal. Thus these interpair correlation effects are quite important and must be included for results of chemical usefulness.

Since an experimental determination of this bond energy would include the difference in zero-point energies of the molecule and fragments, it is necessary to apply a zero-point vibrational energy correction to D_e'. Estimating the vibrational frequencies for $^3A_2$ aminonitrene on the basis of diimide and hydrazine (as shown in Table VI) and using the experimental values of NH_2, we calculate a zero-point correction of 5.5 kcal/mol. Thus we predict that the dissociation energy for $^3A_2$ aminonitrene to $NH_2(^2A_1)$ and $N(^4S)$ is $D_0'(H_2NN)$ = 83.7 kcal/mol.

The calculated heat of formation (of the planar molecule)[16] is

$$\begin{aligned}\Delta H_{f_{0K}}(H_2NN, {}^3A_2) &= \Delta H_f(N, {}^4S) + \Delta H_f(NH_2, {}^2A_1) - D_0' \\ &= 112._5 + (45._3 + 29.3) - 83._7 = 103._4 \text{ kcal/mol}\end{aligned}$$

where $45._3$ is the estimated[16,25] ΔH_{f_0} of NH_2 ($^2B_1$) and 29.3 is the excitation energy[26] from the $^2B_1$ ground state to the $^2A_1$ excited state of NH_2. Using the calculated $^3A_2$–$^1A_1$ separation leads then to

$$\Delta H_{f_{0K}}[H_2NN(^1A_1)] = 88._4 \text{ kcal/mol}$$

which is

$$D_0(H_2NN, {}^1A_1) = 45._3 + 112._5 - 88._4 = 69._4 \text{ kcal}$$

below the energy of the ground state dissociation products, $NH_2 + N$. (As mentioned above, the adiabatic singlet surface dissociates to excited products.) Using our geometry and predicted vibrational frequencies, we find that

$$\Delta H_{f_{298K}}[H_2NN(^1A_1)] = 90._1 \text{ kcal/mol}$$

Thus the energy of $H_2NN(^1A_1)$ is only 14 kcal/mol below that of $N_2 + H + H$, and is 54 kcal/mol above that of diimide **6** [ΔH_f (**6**) = 36 ± 1 kcal/mol[27]]. Assuming that ΔH_f (HN=N·) = ~55 kcal,[28,29] the ΔH for breaking the first N-H bond of $H_2NN(^1A_1)$ is ~17 kcal/mol (there could be a small additional activation energy). Thus, although the $^1A_1$ state of H_2NN is of high energy, it may be possible to form and to detect it.

As indicated in the Introduction, a motivation in this work was to provide some information about the relative energies of 1,2- and 1,1-diazines. In the simplest approximation, one could assume that the 1,1-diazine is 54 kcal above the corresponding 1,2-diazine (since this is the calculated energy of **4** relative to **6**).

An alternative approach is as follows. Since the triplet state of **4** forms a single bond, we might compare this bond strength

$$D(H_2N\text{-}N, {}^3A_2) = 54._4 \text{ kcal/mol}$$

(to ground state products) with the corresponding cases[25]

$$D(H_2N\text{-}H) = 109 \text{ kcal/mol}$$

$$D(H_2N\text{-}CH_3) = 86 \text{ kcal/mol}$$

Assuming the relative bond energies to be the same for other species leads to

$$\Delta H_f(R_1R_2N\text{-}N, {}^3A_2) = \Delta H_f(R_1R_2N\text{-}H) + 116 \text{ kcal/mol}$$

and

$$\Delta H_f(R_1R_2N\text{-}N, {}^3A_2) = \Delta H_f(R_1R_2N\text{-}CH_3) + 110 \text{ kcal/mol}$$

(where 116 = 113.0 − 52.1 − 54. + 109 and 110 = 113 − 34.8 − 54 + 86). To obtain the ground state for the diazine we must subtract the $^1A_1$–$^3A_2$ excitation energy. Methyl substitution should increase this excitation energy since the singlet state has the amino N lone pair delocalized onto the nitrene N, relaxing the interaction with the substituents. We do not have any solid basis for estimating this effect but assume that it might be worth as much as 10 kcal, leading to a total excitation energy of 25 kcal. This leads to

$$\Delta H_f(R_1R_2N{=}N, {}^1A_1) = \Delta H_f(R_1R_2N\text{-}H) + 91 \text{ kcal} \tag{23}$$

$$\Delta H_f(R_1R_2N{=}N, {}^1A_1) = \Delta H_f(R_1R_2N\text{-}CH_3) + 85 \text{ kcal/mol} \tag{24}$$

In addition, cyclic systems will probably have a different strain energy for the 1,1-diazine than for the reference system; however, we will ignore such effects here since there is no basis for quantitative estimates. Thus we would predict

$$\Delta H_f(Me_2N{=}N, {}^1A_1) = 86 \text{ or } 80 \text{ kcal/mol}$$

respectively [probably the estimate from (24), the second choice, is more reliable]. Using the standard thermochemical group contributions[25] [C-(N)(H)$_3$ = −10.08 kcal/mol] suggests a thermochemical contribution for the 1,1-diazo group

Table V. Comparison of Calculated N-N Bond Energies and $^3A_2$-$^1A_1$ Excitation Energies for Different Wave Functions[e]

	$H_2NN(^3A_2)$ planar (R = 1.374 Å)	$H_2NN(^1A_1)$ planar (R = 1.246 Å)	$H_2N(^2A_1)$[b]	$D_e(^3A_2)$,[c] kcal/mol	$\Delta E(^3A_2-^1A_1)$ planar, kcal/mol	$\Delta E(^3A_1-^1A_1)$ adiabatic,[d] kcal/mol
HF	−109.98680	−109.98538[a]	−55.51338	49.6	−0.9	−5.3
GVB(3/7)	−110.01407	−110.03618	−55.5252	59.5	13.9	9.5
GVB(6/15)	−110.05526	−110.08267	−55.55379	64.2[c]	17.2	
GVB(3/7)-CI	−110.0360	−110.0587	−55.5252	73.0	14.2	
GVB(6/15)-CI	−110.08525	−110.10915	−55.54874	89.2	15.0	14.8

[a] R = 1.23 Å. [b] Unless otherwise noted, the N limit is the HF wave function for $N(^4S)$, $E = -54.39441$. [c] $N(^4S)$: $E = -54.3992$. [d] Using the optimum nonplanar geometry for the $^3A''$ state. [e] Note that the triplet wave function is for the optimum *planar* geometry. Energies in hartree atomic units unless indicated otherwise.

Table VI. Vibrational Frequencies Used in Zero-Point Energy Calculation

Vibration		$H_2NN(^3A_2)$	$H_2NN(^1A_1)$ (estd)[a]	$H_2N(^2A_1)$ (exptl)[b]
NH	a_1	3270	3270	3325
	b_2	3340	3340	3325
NH_2	a_1	1294	1294	633
	b_2	1016	1016	
	b_1	873	873	
NN	a_1	1318[c]	1529[d]	
Total zero-point energy, kcal/mol		15.9	16.2	10.4

[a] Based on experimental results in hydrazine; ref 11. [b] Reference 20, the $NH(b_2)$ value is assumed. [c] Estimated from $^1A_1$ using ratio of calculated force constants. The calculated vibrational frequencies are 1236 and 1434 cm^{-1} for $^3A_2$ and $^1A_1$, respectively. [d] From diimide: V. E. Bonybey and J. W. Nibler, *J. Chem. Phys.*, **58,** 2125 (1973).

of

$$\Delta H_f(>N{=}N) = 106 \text{ to } 100 \text{ kcal/mol} \qquad (25)$$

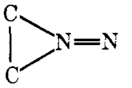
(we will use the latter value). In comparison, Engel[30] has recently suggested that

$$\Delta H_f(\text{Me-N}{=}\text{N-Me}) = 35.5 \pm 1.1 \text{ kcal/mol}$$

indicating that

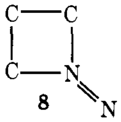
$$\Delta H_f(\text{-N}{=}\text{N-}) = 55.7 \text{ kcal/mol} \qquad (26)$$

Standard thermochemical application of these values[25] leads to (each C indicates a methylene group)



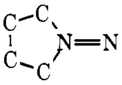
$\Delta H_f = 114$;

7



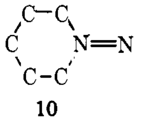
$\Delta H_f = 108$

8



$\Delta H_f = 84$;

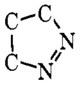
9



$\Delta H_f = 73$

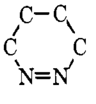
10

which can be compared, for example, with[31,32]



$\Delta H_f = 43.3$;

11



$\Delta H_f = 44$

1

Thus, for example, the isomerization **8** → **11** is expected to be exothermic by 65 kcal, while the isomerization **9** → **1** is expected to be exothermic by 40 kcal. Thus in synthesizing a 1,1-diazine, **9** might be a more suitable goal than **8.** Comparing $\Delta H_f = 84$ for **9** with the ΔH_f of the tetramethylene biradical (62 kcal/mol),[25] the exothermicity for blowing the N_2 out of piperidine nitrene **9** is estimated as 22 kcal/mol. Such types of estimates should be useful in understanding the thermal rearrangements and reactions of nitrenes. For example, the activation energy for ring opening of **1** is ~34 kcal,[33] indicating that breaking a CN bond of **9** is 7 kcal exothermic. There may still be an activation barrier for opening the ring of **9**; however, **9** would appear likely to not be very stable.

These discussions and predictions of ΔH_f involve a number of uncertainties; however, it is hoped that they will be illustrative of the energetics of diazines.

B. Dipole Moments. In GVB wave functions the orbitals are unique and localized with chemically identifiable characteristics, making it useful to analyze properties such as dipole moments in terms of orbital contributions. In order for the dipole moment to be independent of origin we associate with the electron of each orbital a unit nuclear charge centered at the nucleus on which the orbital is centered (in the VB model). This leads to the results shown in Table IV.

The dipole moment of the $^3A_2(\pi\bar{\pi})$ state is dominated by the nitrene-nitrogen 2s pair which hybridizes away from the molecule owing to formation of the NN σ bond. This orbital leads to a dipole moment of 2.68 D (nitrene end negative), while the other orbitals lead to 0.33 D in the opposite direction, resulting in a total dipole moment of 2.35 D.

For the $^1A_1(\bar{\pi}^2)$ state the major change from $^3A_2$ is the extensive delocalization of the amino π pair due to the lack of nitrene π electron. Thus the π system of $^1A_1$ has an increased dipole moment of 3.30 D. In response to this shift of π charge to the right, the σ orbitals all shift charge back to the left. The net increase in dipole moment for $^1A_1$ is 1.69 D leading to a total μ of 4.04 D.

It would be hoped that such analyses will lead to construction of transferable bond dipoles useful in predicting dipole moments of molecules. One of the limits on such procedures can be seen in Table IV where the NH dipole is 0.358 D at an angle of 73.6° with the NN axis in $^3A_2$ and 0.486 D at an angle of 54.0° in $^1A_1$ (the NH bond angle is 57.7°). It is not immediately obvious how one could predict the dipoles for the $^3A_2$ case knowing the values for the $^1A_1$ state.

C. Inversion Barrier. As in NH_3, the amino N is generally nonplanar and hence for the $^3A_2(\pi\bar{\pi})$ state, we carried out calculations to determine the geometry and energy barrier. with the GVB(3/7) wave function we found a pyramidal geometry (the angle between the H_2N plane and the NN axis being 42.2°, tetrahedral would be 54.7°) with an inversion barrier of 4.4 kcal/mol. For comparison, NH_3 has an angle[16] of 61.3° and a barrier of 5.8 kcal/mol, while H_2N-NH_2 has pyramidal angles[16] of 49.6° and a barrier[16] of 2.8 kcal/mol. With minimum basis HF, Pople et al.[7] found a pyramidal geometry for H_2NN of 36.6°. Using an extensive basis and complete geometry optimization, Ahlrichs[9] obtained an optimum pyramidal angle of 42° and an inversion barrier of 2.7 kcal. However, including all the correlation effects for the GVB(6/13)-CI at the planar and optimum pyramidal geometries leads to a very flat potential curve. The calculations give an optimum angle of 21° and an inversion barrier of 0.2

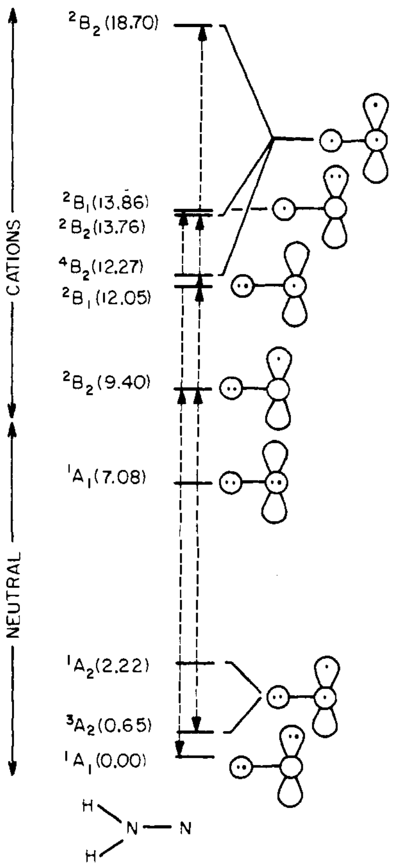


Figure 5. Electronic states of aminonitrene and aminonitrene cation. Energies in electron volts (1 hartree = 27.2116 eV = 627.5096 kcal/mol). The arrows on the dotted lines show which ion states are obtained directly from each state.

kcal/mol; however, the grid used is too crude for accurate results.

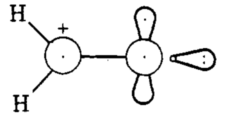
Because of the strong π bonding of $^1A_1(\bar{\pi}^2)$ we assumed that the geometry is planar and did not carry out calculations of the inversion barrier.

D. Comparison with Other Calculations. Ahlrichs[9] has carried out extensive ab initio HF calculations on the $^1A_2$ and $^3A''$ states. For the singlet state the calculated geometry is $R_{NN} = 1.22_2$ Å, $R_{NH} = 1.01_6$ Å, and $\angle HNH = 114°$, in reasonable agreement with the value $R_{NN} = 1.24_6$ Å we calculated for our correlated wave function (we assumed $R_{NH} = 1.016$ Å and $\angle HNH = 115.4°$). For the triplet state they obtain $R_{NN} = 1.34$ Å, $R_{NH} = 1.00$ Å, $\angle HNH = 113°$, and $\theta = 42°$, whereas we calculated 1.37_4 Å and $\theta = 42°$ for the GVB wave functions.

From HF calculations Ahlrichs found the triplet state to be 5.2 kcal below the singlet, in good agreement with our HF result of 5.3 kcal. Ahlrichs[9] carried out approximate electron-correlation calculations (IEPA-PNO[9]), obtaining a triplet ground state with the singlet 2-3 kcal/mol higher. However, we find that explicit inclusion of electron correlation inverts the ordering, leading to the singlet state 15 kcal below the triplet. As indicated in Table V, the major problem with HF is the very poor description of the π bond in the $^1A_1$ state. This one correlation is responsible for a differential lowering of $^1A_1$ with respect to $^3A_2$ by 11.7 kcal (see Table I).

E. Ionization Potentials. The first ionization from $^1A_1(\bar{\pi}^2)$ is out of the doubly occupied $\bar{\pi}$ orbital, leading to a $^2B_2$ ion at 9.4 eV (see Table II and Figure 5). Ionizing an electron from the π (bonding) orbital leads to the $^2B_1$ state at 13.9 eV. These are the only two low-lying states arising from ionization of $^1A_1(\bar{\pi}^2)$; however, a number of states arise from $^3A_2(\pi\bar{\pi})$ as discussed next.

The lowest $^2B_1$ ion state is also obtained from $^3A_2(\pi\bar{\pi})$ by ionization of the unpaired π electron (8.8 eV, indicating the effect on the amino lone pair on this orbital). Ionization of the electron out of the π orbital of the $^3A_2$ state costs 11.4 eV, resulting in a $^2B_1$ ion at 12.1 eV above $^1A_1$. Ionization of an electron from the doubly occupied π lone pair of the $^3A_2$ state results in three ion states all having the same spatial configuration:



leading to a quartet state and two doublets. Singlet coupling of the two π electrons to yield a π bond results in a $^2B_2$ state at 13.8 eV (13.1 eV above $^3A_2$). The remaining two states have triplet pairing of the π and $\bar{\pi}$ orbitals, leading to $^4B_2$ at 12.3 eV and $^2B_2$ at 18.7 eV.

VI. Summary

We find that the ground state of aminonitrene is the singlet state ($^1A_1$) with a triplet state ($^3A_2$) at 14.8 kcal/mol. This stabilization of the singlet state is due to a large amount of double bond character in the NN bond.

We find the nitrogen-nitrogen bond dissociation energy (to ground state products) for the $^1A_1$ ground state of aminonitrene to be 69 kcal/mol, leading to $\Delta H_{f_{0K}}$ of 88 kcal/mol and $\Delta H_{f_{298K}} = 90$ kcal/mol. The dipole moment is found to be 4.036 D for the $^1A_1$ state and 2.351 D for the $^3A_2$ state of aminonitrene. The ionization potential in $H_2NN(^1A_1)$ is calculated to be 9.4 eV.

The various properties of the states of aminonitrene are quite consistent with the GVB model for this molecule.

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A Study of One-Electron Functionals for Molecular Correlation Energies

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Abstract: The Carr–Gordon–Kim electron correlation functional is applied to a series of hydrides for C, O, N, and F, and to a selection of small molecules using several basis sets. Excellent agreement of calculated correlation energies with experiment is generally found and the results are essentially independent of the basis set used. Calculated correlation energies for successive reactions of C, N, O, and F with H are in good agreement with experimental values. The results indicate that one-electron density functionals show promise for the economical estimation of electron correlation energies of large molecular systems.

In recent years, ab initio molecular orbital (MO) calculations have been applied even to relatively large molecular systems, such as those common in organic chemistry. These calculations have generally been of the single-determinant LCAO-MO-SCF type for which a specific limitation is set on the energy by the variational principle. The difference between this lower bound, the Hartree–Fock limit, and the true or experimental energy is the correlation energy, a relatively large quantity (many eV) that is often not considered explicitly.

The successful treatment of isodesmic reactions even with minimal basis sets[2,3] demonstrates that correlation energy differences can be quite small for closed shell systems having equal numbers of similar kinds of bonds. However, where bonds are broken, or severely altered, as in the study of reaction transition states, this approach may be less satisfactory, and explicit consideration of the correlation energy may be required. For large molecular systems the application of configuration interaction (CI) techniques becomes prohibitively expensive.

Correlation energies have been related to the numbers and types of electrons as in the IEPA (independent electron pair approximation)[4] and the CEPA (coupled electron pair approximation)[5] methods. While one may obtain disastrous[5] results with the former, accurate variational type correlation energies may be obtained with the latter method, at a cost somewhat less than that of a good CI, but this method too can become time consuming for large systems. Recently, however, the use of functionals has been reintroduced[6-9] as an alternative to CI methods.

The procedure considered here represents the correlation energy (CE) as a functional $f(\rho)$ of the self-consistent field (SCF) single-determinant electron density distribution, ρ. A rather simple analytical, one-electron function of ρ is typically used for $f(\rho)$, particularly if ρ is slowly varying.

$$F \approx \int \rho f(\rho) d\tau \quad (1)$$

Furthermore, if the function itself varies slowly with ρ, then ρ might be well enough approximated with rather limited LCAO basis sets, e.g., Slater orbitals, whose SCF energy may in fact be rather far from the Hartree–Fock limit. In principle, eq 1 can be applied to systems containing two or more electrons with rather unsophisticated computational effort.

Wigner first proposed that such a functional should exist[9] and Slater[10] successfully used a functional dependent on $\rho^{1/3}$ to calculate exchange energies, which are a type of correlation energy (i.e., the difference in energy between a simple product wave function and an antisymmetrical one).

Of course, electron correlation is a two-electron phenomenon and recently a two-electron functional has been shown to provide excellent evaluations of correlation energies for small molecules.[11] In this paper we explore the possible application of one-electron functions to simple open and closed shell molecular systems with an eye to treating larger organic systems. We also are interested in a functional that is of an intensive nature rather than having a mixture of intensive and extensive character. We discuss briefly two different such functionals that have been proposed in the literature,[6-8] indicate some limitations, propose some changes, and finally show that these functionals can give satisfactory estimates of molecular correlation energies under the specified conditions.

Lie–Clementi (LC) Functional. Lie and Clementi[8] have recently explored the use of a functional first given by Gombas.[12,13]

$$f(\rho) = a_1\rho^{1/3}(a_2 + \rho^{1/3})^{-1} + b_1 \ln (1 + b_2\rho^{1/3}) \quad (2)$$

Lie and Clementi parameterized eq 2 using atomic SCF-LCAO-MO's to fit the correlation energies for the closed shell atoms He, Be, and Ne. Consideration was next given to the fact that an unpaired electron contributes less to the total correlation energy than it would if its orbital were doubly occupied. Lie and Clementi generalized eq 1 by replacing the electron density with the LCAO expansion