other kind of possible structures of a five-coordinate compound, "square pyramids", is the transition state for rearrangement connecting the "trigonal-bipyramidal" equilibrium structures. The transition-state structures indicate that the rearrangement occurs via the Berry pseudorotation mechanism. The intrinsic activation barrier for Berry pseudorotation is calculated to be only a few kcal/mol. The potential energy surface for olefin coordination to $Rh(H)(CO)_2(PH_3)$ has been investigated as well. As expected, the electron correlation is very important in determining this energetics. We have also determined the transition structures for intramolecular olefin insertion of $Rh(H)(C_2H_4)(CO)_2(PH_3)$. The reaction starts from the most stable isomers of the olefin complex with axial H and equatorial ethylene and goes through an early transition state with basal H and basal ethylene in which Rh—H is parallel to the C=C bond, before reaching the square-planar ethyl complex. The activation barrier is calculated at the RHF level to be 20–21 kcal/mol. This barrier is higher than that calculated previously for group 10 complexes. The origin of the activation barrier is ascribed to the change of the skeleton to the square pyramidal.

As has been discussed in the introduction, the overall goal of the present project is to calculate the potential energy profile of the entire catalytic cycle presented in Scheme II and to provide insight into the nature and the controlling factors of the catalytic system. In the present paper, we have covered only two steps in the catalytic cycle. Combining the results for olefin coordination and rearrangement in Figure 1 and for olefin insertion in Figure 3, one can find that there are three favorable direct paths from $Rh(H)(CO)_2(PH_3)$ (**3**) through $Rh(H)(C_2H_4)(CO)_2(PH_3)$ (**1**) to $Rh(C_2H_5)(CO)_2(PH_3)$ (**2**).

$$\begin{array}{lllll}
\mathbf{3b} & \rightarrow \mathbf{1a} & \rightarrow (\mathrm{TS}) & \rightarrow & \mathbf{2a} \\
(29.9) & 0.0 & 23.4 & & (-13.5)\ \mathrm{kcal/mol} \\
\\
\mathbf{3a} & \rightarrow \mathbf{1b} & \rightarrow (\mathrm{TS}) & \rightarrow & \mathbf{2b} \\
28.2 & 3.4 & (24.0) & & (-11.7)\ \mathrm{kcal/mol} \\
 & & \rightarrow (\mathrm{TS}) & \rightarrow & \mathbf{2a} \\
 & & (25.2) & & (-13.5)\ \mathrm{kcal/mol}
\end{array}$$

The numbers are relative energies in kcal/mol at the MP2 level, with those in parentheses representing an MP2 estimate from the RHF calculation. In all these paths, the energetics is comparable and the mechanism is similar; **3** goes with no or a small barrier to the most stable isomers of **1**, which, without any rearrangement among isomers of **1**, climb up a substantial barrier and then exothermically reach **2**. It is also possible for **3** to form **1d** or **1e**, which then have to rearrange through the BPR to isomers **1a** or **1b**, respectively, before olefin insertion can take place to yield **2**. Studies on the other steps of the catalytic cycle will continue in our laboratory.

Acknowledgment. The authors acknowledge Drs. R. L. Martin and P. J. Hay for providing an effective core potential subroutines. All the calculations were carried out at the Computer Center of Institute for Molecular Science.

Registry No. 1, 113860-09-6; $Rh(H)(CO)_2(PH_3)$, 113975-04-5.

Supplementary Material Available: Tables of full optimized geometrical parameters for all the equilibrium and the transition structures (12 pages). Ordering information is given on any current masthead page.

Computational Evaluation and Comparison of Some Nitramine Properties

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Abstract: A computational study of six nitramines, $R_1R_2NNO_2$, has been carried out with the objective of gaining a better understanding of how the properties of the NNO_2 group are affected by the natures of R_1 and R_2. An ab initio SCF procedure was used, with the initial step being the determination of each molecule's optimized geometry. This was subsequently used to compute its bond orders, dipole moment, and electrostatic potential. In most instances, the NNO_2 portions of the molecules are planar, due to the strong electron-withdrawing effect of the nitro group; the amino-type nitrogen can better respond to this when in a planar configuration. One consequence is that the $N-NO_2$ bonds possess some degrees of double bond character; their bond orders range from 1.36 to 1.63, with the weaker bonds corresponding to the more electron-withdrawing R_1 and R_2 groups. The strong negative electrostatic potentials normally associated with the lone pairs of amino-type nitrogens are greatly weakened or eliminated in most of these molecules; several of them show evidence of significant hyperconjugation, resulting in enhanced acidic character.

There is a considerable amount of interest in nitramines, $R_1R_2N{+}NO_2$, as high-energy compounds.[1-10] For example, two of the currently most effective secondary explosives are 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, I) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, II).[11] It is particularly important. for these and related systems, to develop greater insight into the factors that affect their stabilities toward chemical agents, heat, and shock or impact.

In order to better understand how the properties of the NNO_2 group are influenced by the natures of the attached R_1 and R_2,

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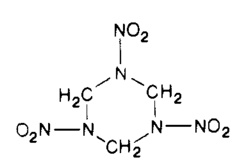
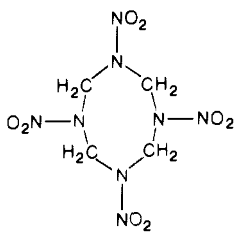


I

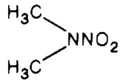


II

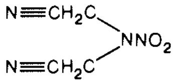
we have carried out a computational study of the six systems III–VIII. Two of these—ethylenedinitramine (VI) and nitroguanidine (VII), which is a nitrimine—have been used extensively as explosives.[11]

H_2NNO_2

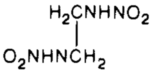
III



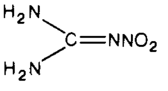
IV



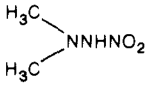
V



VI



VII



VIII

The mechanisms of decomposition of nitramines, and particularly the question as to whether N–N or C–N bond breaking is the more important in any given instance, have been the subjects of many investigations and discussions.[2,8-10,12-14] We shall not address these issues in this paper, although we have found empirical evidence linking the shock sensitivities of nitramines to properties of the N–N bonds.[15] Our present analysis centers upon (a) the molecular electrostatic potentials of III–VIII, as guides to the charge distributions and chemical reactivities of these molecules, and (b) their bond orders, as indicators of the relative strengths of the various bonds.

Methods

1. General Approach. The first step in the study of each molecule was the calculation of its optimized geometry with the ab initio self-consistent-field GAUSSIAN 82 program at the 3-21G level.[16] This basis set has been shown to be effective for structure determinations.[17]

The optimum 3-21G geometry was used in computing the bond orders and electrostatic potential of each molecule. For the bond orders, which require time- and space-consuming vibration frequency calculations, the STO-3G basis set was used; for a given type of bond, the bond orders obtained at this level are very similar in their relative magnitudes to the 3-21G results.[18] The electrostatic potentials were computed with the STO-5G basis set, which is energetically superior to the 3-21G and which we have found to yield reliable potentials.

2. Bond Orders. We have demonstrated that bond orders calculated with eq 1 correlate well with experimentally determined bond dissociation energies.[19] In eq 1 k is the force constant in

$$\text{bond order} = 0.55747(k/R)^{1/2} \tag{1}$$

mdyn/A and R is the equilibrium bond length in Å; we obtain both quantities computationally, with the GAUSSIAN 82 program. These bond orders are an effective means for predicting relative bond strengths, particularly for a given type of bond (e.g., N–N) in different environments.

3. Electrostatic Potentials. The electrostatic potential $V(\vec{r})$ that is created at any point $\vec{r}$ in the space around a molecule by its nuclei and electrons is given rigorously by eq 2. Z_A is the

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')d\vec{r}'}{|\vec{r}' - \vec{r}|} \tag{2}$$

charge on nucleus A, located at $\vec{R}_A$, and $\rho(\vec{r})$ is the electronic density function of the molecule, which we compute from the STO-5G molecular wave function.

The electrostatic potential is well established as an effective tool for understanding and predicting molecular reactive behavior.[20-22] For example, an approaching electrophile is initially attracted to regions of negative potential (especially to the points at which are found the local minima, where $V(\vec{r})$ has its most negative values), since these are where the effects of the molecule's electrons are dominant. A key feature of the electrostatic potential is that it is a real physical property and can be determined experimentally as well as computationally.[22]

Results

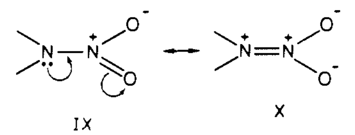
The 3-21G optimized geometries for III–VIII are given in Table I. In general, they are in good agreement with the available experimentally determined structural data. Molecules III–VII are essentially planar, except for the methyl and methylene hydrogens in IV–VI and the CN groups in V. Ethylenedinitramine, as would be anticipated for steric reasons, prefers the anti–staggered conformation, as shown in VI. In VIII, while the atoms in the NNO_2 portion are coplanar, the two amino-type nitrogens have distinctly nonplanar configurations. This will be discussed further in the next section.

Table II presents the energies and dipole moments as computed at both the 3-21G and STO-5G levels (with the 3-21G optimized structures). The STO-5G basis gives better energies, reflecting its larger number of Gaussian functions. The STO-5G dipole moments also appear to be the more accurate, judging from the two experimentally measured values that are available. This provides support for our calculating the electrostatic potential (a one-electron property, like the dipole moment) at the STO-5G level.

The bond orders for molecules III–VIII are listed in Table III. Finally, the calculated electrostatic potentials in various planes through these systems are shown in Figures 1–8.

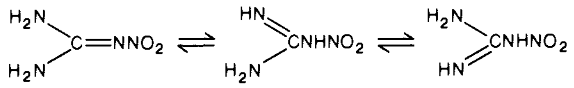
Discussion

1. Structures. The fact that the NNO_2 portions of molecules III–VI are essentially planar can be attributed to the strong electron-withdrawing power of the nitro group. We have observed earlier that this induces an NH_2 substituent to assume a planar configuration, as shown in structure X, in which it can better donate electronic charge in response to this demand.[23-25]



IX X

Molecules VII and VIII present structural features of special interest. Nitroguanidine, VII, can have several tautomeric forms, as shown below. We found VIIa to be the most stable, and



VIIa VIIb VIIc

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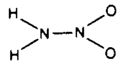
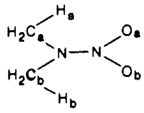
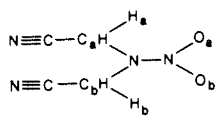
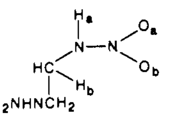
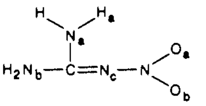
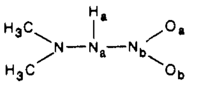
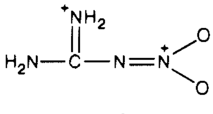
Table I. Calculated Structures[a]

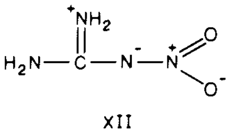
molecule	distances, Å	angles, deg
 III	N-N: 1.354 N-O: 1.247 N-H: 0.995 O···H: 2.36	O-N-O: 127 N-N-O: 116 H-N-N: 116 H-N-H: 128
 IV	N-N: 1.345 (1.323) N-O$_a$: 1.258 (1.243) N-O$_b$: 1.257 (1.233) C-N: 1.463 (1.459) (1.436) C$_a$-H$_a$: 1.074 C$_b$-H$_b$: 1.078 C-H: 1.078-1.083 O$_a$···H$_a$: 2.19 O$_b$···H$_b$: 2.48	O-N-O: 125 (123.4) N-N-O$_a$: 119 (118.3) N-N-O$_b$: 116 (118.3) N-N-C$_a$: 119 (117.9) N-N-C$_b$: 116 (117.2) N-C$_a$-H$_a$: 108 N-C$_b$-H$_b$ 110 N-C-H: 107-111 H-C-H: 109-110
 V	N-N: 1.371 N-O$_a$: 1.247 N-O$_b$: 1.246 C$_a$-N: 1.457 C$_b$-N: 1.456 C-C: 1.463 C≡N: 1.138 C$_a$-H$_a$: 1.076 C$_b$-H$_b$: 1.077 C-H: 1.081 O$_a$···H$_a$: 2.17 O$_b$···H$_b$: 2.21	O-N-O: 126 N-N-O: 117 N-N-C: 118 N-C$_a$-H$_a$: 108 N-C$_b$-H$_b$: 109 N-C-H: 108 C$_a$-N-C$_b$: 123 N-C$_a$-C: 111 N-C$_b$-C: 111 H-C-H: 109
 VI	N-N: 1.350 (1.301) N-O$_a$: 1.250 (1.236) N-O$_b$: 1.251 (1.240) C-N: 1.457 (1.463) C-C: 1.530 (1.529) N-H: 0.998 C-H: 1.080 O$_a$···H$_a$: 2.32 O$_b$···H$_b$: 2.55	O-N-O: 127 (123.0) N-N-O$_a$: 117 (119.5) N-N-O$_b$: 116 (117.5) C-C-N: 108 (110.2) C-N-N: 119 (122.9) H-N-N: 114 C-N-H: 128 H-C-H: 109
 VII	N$_c$-N: 1.377 (1.354) N-O$_a$: 1.287 (1.260) N-O$_b$: 1.227 (1.226) C-N$_a$: 1.329 (1.308) C-N$_b$: 1.343 (1.328) C-N$_c$: 1.325 (1.359) N$_a$-H$_a$: 1.003 (0.957) N$_a$-H: 0.995 (1.001) N$_b$-H: 0.994 (0.960) 0.997 (0.980) O$_a$···H$_a$: 1.81	O-N-O: 122 (119.9) N$_a$-C-N$_c$: 128 (128.5) N$_b$-C-N$_c$: 114 (111.2) C-N$_c$-N: 119 (119.5) N$_c$-N-O$_a$: 122 (122.6) N$_c$-N-O$_b$: 115 (117.4) N$_a$-C-N$_b$: 118 (120.1) C-N$_a$-H$_a$: 116 (120.6) H-N$_a$-H$_a$: 122 (118.4) H-N$_b$-H: 120 (125.4) C-N$_a$-H: 122 (120.9) C-N$_b$-H: 118 (115.3) 123 (119.2)
 VIII	N$_a$-N$_b$: 1.412 N-N$_a$: 1.399 N-O$_a$: 1.252 N-O$_b$: 1.224 N$_a$-H$_a$: 1.006 C-N: 1.467 C-H: 1.078-1.089 O$_a$···H$_a$: 2.25	O-N-O: 128 N$_a$-N$_b$-O$_a$: 113 N$_a$-N$_b$-O$_b$: 119 N-N$_a$-N$_b$: 115 C-N-C: 117 H$_a$-N$_a$-N$_b$: 107 N-C-H: 108-113 H-C-H: 108-110

[a] Experimentally determined distances and angles are given in parentheses for IV, VI, and VII. The sources are as follows. IV: Filhol, A.; Bravic, G.; Rey-Lafon, M.; Thomas, M. *Acta Crystallogr. B* **1980**, *36*, 575. VI: Turley, J. W. *Acta Crystallogr. B* **1968**, *24*, 942. VII: Choi, C. S. *Acta Crystallogr. B* **1981**, *37*, 1955.

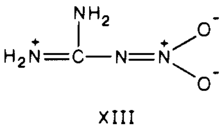
experimental evidence indicates that this is the form that is present in the solid state.[11,26,27] However our calculations reveal that all three C-N bonds have a considerable amount of double-bond character and actually are extremely similar in terms of both length and bond order (Tables I and III). Apparently there are significant contributions from resonance structures such as XI-XIV, although the N-N bond order of 1.43 shows that the roles of XI and XIII are not as important as are those of resonance contributors of type X in the cases of molecules III-VI, in which the N-N bond orders are between 1.53 and 1.63.



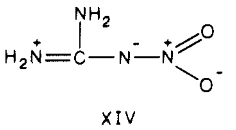
XI



XII



XIII



XIV

The nonplanarity of the middle nitrogen in VIII suggests that the contribution of X is much less in this system; this is also evident from the calculated bond lengths and bond orders (Tables I and III). A possible explanation is that the delocalization of this nitrogen's lone pair toward the NO_2 group (see IX and X) is opposed by the strong inductive attraction of the $(H_3C)_2N$ group, thus diminishing the role of X. As a result, VIII has the weakest $N-NO_2$ bond encountered in this study, with a bond order of only 1.36.

Table II. Calculated Energies and Dipole Moments[a]

	energies, hartrees		dipole moments, debyes		
molecule	STO-5G	3-21G	STO-5G	3-21G	exp
H_2NNO_2 (III)	258.457	−258.138	3.52	4.66	3.78[b]
$(H_3C)_2NNO_2$ (IV)	−336.329	−335.775	4.06	5.32	4.61[c]
$(NCCH_2)_2NNO_2$ (V)	−519.075	−518.188	1.60	2.21	
$O_2NHNCH_2CH_2NHNO_2$ (VI)	−593.632	−592.756	0.02	0.02	
$(H_2N)_2C{=}NNO_2$ (VII)	405.838	−405.261	6.71	8.30	
$(H_3C)_2NNHNO_2$ (VIII)	−391.124	−390.448	4.26	5.46	

[a] The STO-5G energies and dipole moments are computed by using the 3-21G optimized geometries. [b] McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963. [c] George, M. V.; Wright, G. F. *J. Am. Chem. Soc.* **1958**, *80*, 1200.

2. Intramolecular Hydrogen Bonding. If an O···H separation that is less than the sum of the oxygen and hydrogen van der Waals radii (1.4 and 1.2 Å, respectively[28]) is interpreted as evidence of intramolecular hydrogen bonding, then it is occurring in each of the nitramines being discussed in this paper. In most instances it is rather weak, the O···H distance being 2.2 Å or more; however, a notable exception is in nitroguanidine (VII), in which there is an O···H separation of 1.81 Å, indicating a relatively strong interaction.

Tables I and III show that a general consequence of this intramolecular hydrogen bonding is a significant lengthening and weakening of the corresponding N-O bonds, their bond orders decreasing from about 2.0 to roughly 1.8 and even, in VII, to 1.57. The effects upon the C-H or N-H bonds that are involved are much weaker and opposite in nature; the former become slightly

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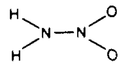
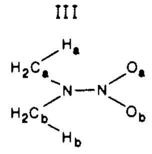
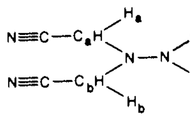
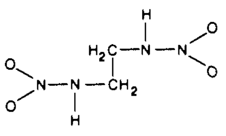
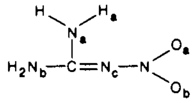
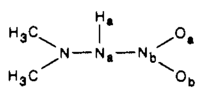
(28) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table III. Calculated Bond Orders

molecule	bond orders
 III	N-N: 1.59 N-O: 1.83 N-H: 1.84
 IV	N-N: 1.63 N-O_a: 1.74 N-O_b: 1.76 C-N: 1.27 C_a-H_a: 1.53 C_b-H_b: 1.51 C-H: 1.48-1.51
 V	N-N: 1.53 N-O_a: 1.82 N-O_b: 1.83 C-N: 1.28 C-C: 1.25 C≡N: 2.83 C_a-H_a: 1.52 C_b-H_b: 1.52 C-H: 1.49
 VI	N-N: 1.60 N-O: 1.81 C-N: 1.29 C-C: 1.17 N-H: 1.82 C-H: 1.50
 VII	N_c-N: 1.43 N-O_a: 1.57 N-O_b: 2.03 C-N_a: 1.65 C-N_b: 1.62 C-N_c: 1.62 N_a-H_a: 1.76 N_a-H: 1.83 N_b-H: 1.82, 1.83
 VIII	N_a-N_b: 1.36 N-N_a: 1.41 N-O_a: 1.80 N-O_b: 2.01 N_a-H_a: 1.77 C-N: 1.27 C-H: 1.45-1.51

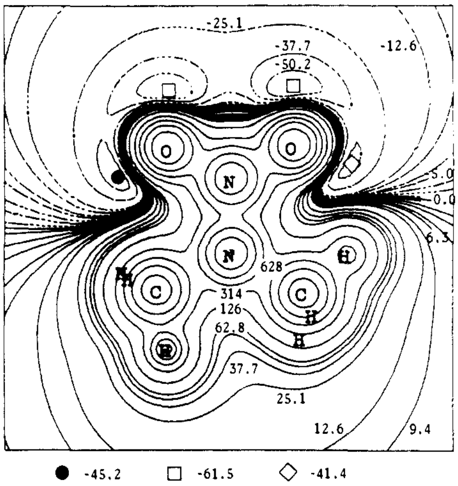


Figure 1. Calculated electrostatic potential of dimethylnitramine (IV) in the molecular plane. Positions of the nuclei, or their projections in this plane, are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

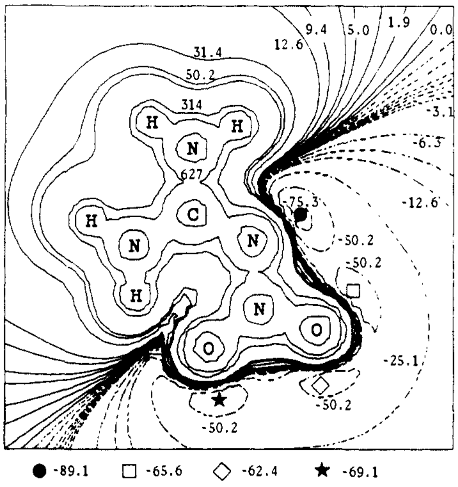


Figure 2. Calculated electrostatic potential of nitroguanidine (VII) in the molecular plane. Positions of the nuclei are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

stronger, while the latter are weakened.

3. N-NO_2 Bond Orders. The strength of the N-NO_2 bond, which we measure by its calculated bond order, depends upon the degree of double-bond character that is introduced by resonance contributors such as X, XI, and XIII; this in turn is influenced by the natures of the groups attached to the amino nitrogen. Thus, taking III as a reference point, it is seen that the electron-withdrawing CN substituents in V weaken the N-NO_2 bond, presumably by opposing the delocalization of the amino lone pair toward the NO_2 group (as in IX and X). This is a weak manifestation of what occurs more strongly in VIII (in which the electron-attracting effect is not diminished by intervening CH_2 groups) and has been discussed earlier in this paper. On the other hand, the electron-donating CH_3 groups in IV slightly strengthen the N-NO_2 linkage.

4. Electrostatic Potentials. In general, the major regions of negative electrostatic potential in molecules III-VIII are associated with the oxygens of the nitro group. These negative potentials are strongest in the NO_2 plane, but do extend well above and below it. Typically, there are four local minima in these regions, as shown for example in Figure 1 for dimethylnitramine (IV).

Normally one also expects to find negative potentials near amino-type nitrogens, due to their lone pairs. These potentials are particularly strong when the configuration around the nitrogen is pyramidal, but can be quite sizable even for planar geometries. For example, NH_3 has a single strong negative region with a minimum of −110 kcal/mol in its equilibrium pyramidal configuration, which is converted into two regions with minima of −57 kcal/mol when the molecule is forced to be planar (they are located near the nitrogen, above and below the plane).[24]

Due to the strong electron-withdrawing power of the NO_2 group, these negative amino potentials are drastically weakened or even eliminated in molecules III-VII (in all of which the amino-type nitrogen has a planar configuration). The strongest such potential is found in H_2NNO_2, III, with minima of −10 kcal/mol above and below the amino nitrogen; in IV-VII, the minima—if even present—are in the neighborhood of −1 kcal/mol. Similar effects have been observed earlier, in a study of the nitroanilines.[23]

Molecule VIII is an exception to the pattern that has just been described for III-VII. Both amino-type nitrogens in VIII have pyramidal configurations, with relatively strong negative potentials that reach −67.3 kcal/mol near the methylated nitrogen and −44.5 kcal/mol near the other. (The nonplanarity of this molecule has been discussed earlier in this paper.) Thus both of these nitrogens should show a considerable degree of basic character.

Another special case is the imine nitrogen in nitroguanidine, VII. Figure 2 shows that it has a strong negative lone pair potential, centered in the molecular plane, which overlaps with the negative regions due to the NO_2 oxygens.

It is of particular interest to examine the electrostatic potentials above the NNO_2 planes of these nitramines, because of what is

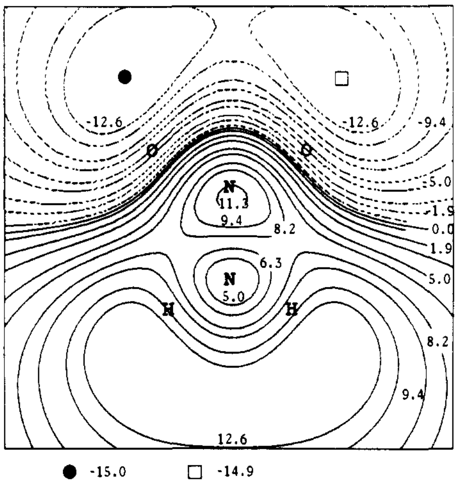


Figure 3. Calculated electrostatic potential of molecule III, 1.75 Å above the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

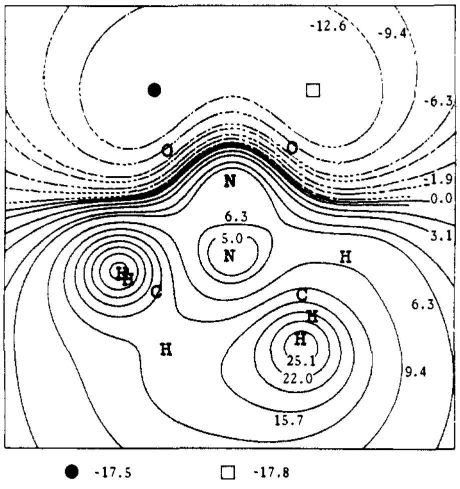
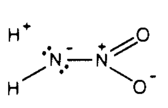
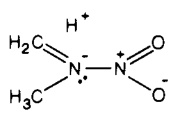


Figure 4. Calculated electrostatic potential of dimethylnitramine (IV), 1.75 Å above the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

revealed about their charge distributions. Several of these molecules show a planar maximum above the NO_2 nitrogen and a planar (positive) minimum above the amino-type nitrogen (see Figures 3–6). They are most positive in V, reflecting the inductive effect of the CN groups.

These maxima can readily be explained in terms of structures IX and X as indicating the positive characters of the NO_2 nitrogens. The planar minima above the amino-type nitrogens suggest hyperconjugative contributions by structures such as XV and XVI,[29] supporting an earlier proposal by Stals.[2] The acidic properties of nitramines[30] can be attributed to these latter effects, as can also the facile exchange of amino hydrogens with deuterium.[31]


XV


XVI

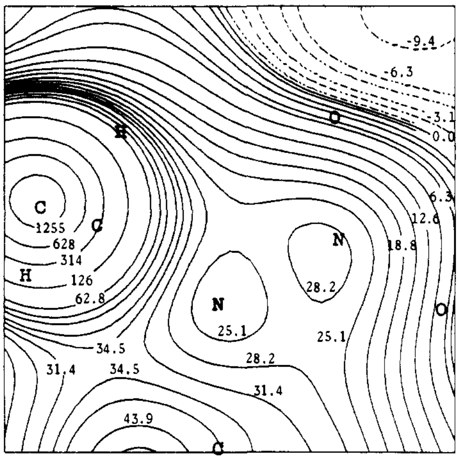


Figure 5. Calculated electrostatic potential of molecule V, 1.75 Å above the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole.

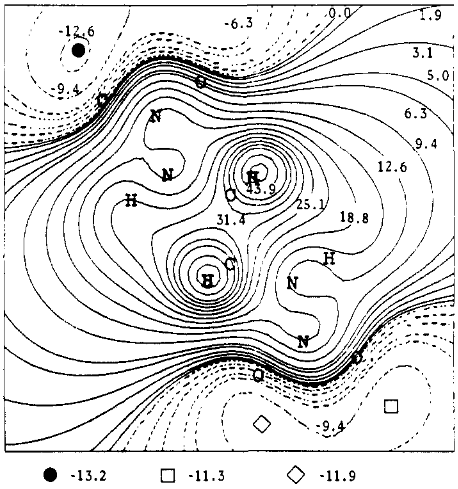


Figure 6. Calculated electrostatic potential of ethylene dinitramine (VI), 1.75 Å above the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

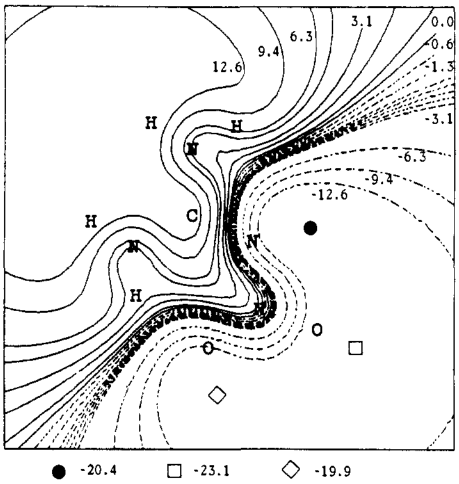


Figure 7. Calculated electrostatic potential of nitroguanidine (VII), 1.75 Å above the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

The situation is quite different in molecules VII and VIII (Figures 7 and 8). It was already pointed out that the imine

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[29] We express our appreciation to Dr. Ieva Ruks Politzer for suggesting this interpretation.

[30] Fauth, M. I.; Frandsen, M.; Havlick, B. R. *Anal. Chem.* **1964**, *36*, 380.

[31] Hampson, P.; Mathias, A. *Chem. Commun.* **1968**, 825.

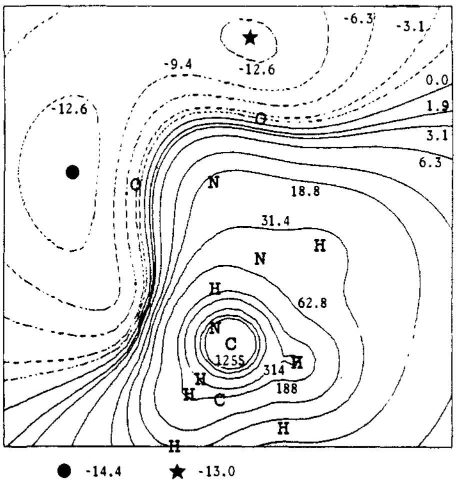

Figure 8. Calculated electrostatic potential of molecule VIII, 1.75 Å above the plane of the NNO_2 portion. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kilocalories/mole. The locations of the most negative potentials in this plane are shown, and their values are given at the bottom of the figure.

nitrogen in VII has a strongly negative lone pair potential; it is centered in the molecular plane, but is still clearly apparent at 1.75 Å above this plane, where it extends above the nitrogen.

In VIII, the nonplanarity of the amino-type nitrogens indicates the absence of any strong contribution from structure X. The strongly negative lone pair potentials associated with these nitrogens have already been mentioned earlier in this discussion.

Summary

An important factor in determining the properties of the nitramines that we have studied is the planarity of the key portion of each molecule except VIII. In most instances, this planarity can be regarded as being due to the strong electron-withdrawing power of the NO_2 group, to which the molecule responds by the rearrangement depicted in structures IX and X. This introduces some degree of double-bond character into the $N-NO_2$ bond, its calculated bond order varying between 1.53 and 1.63 for the more typical nitramines, III–VI; it is 1.43 for the nitrimine VII and 1.36 for VIII, in which the amino-type nitrogens do not have planar configurations. Thus the $N-NO_2$ bond is weakest in these two latter molecules.

The planarity of the amino-type nitrogens in III–VII, in conjunction with the electron-withdrawing effect of NO_2, also result in the near elimination of the strong negative electrostatic potentials normally associated with the lone pairs of amino nitrogens. However, the imine nitrogen in VII and the pyramidal amino-type nitrogens in VIII do retain strong negative lone pair potentials.

An interesting feature of the nitramines III–VI is the indication of a significant hyperconjugative effect. This is revealed by the calculated electrostatic potentials in the regions above the molecular planes. The implication of enhanced acidic character is in accord with the experimentally observed properties of nitramines.

Acknowledgment. We greatly appreciate very helpful discussions with Dr. Ieva Ruks Politzer and Dr. Jack W. Timerlake. We are also grateful to the Office of Naval Research for its support of this work through Contract N00014-85-K-0217.

Band Structures of Polyfulvene and Related Polymers. A Model for the Effects of Benzannelation on the Band Structures of Polythiophene, Polypyrrole, and Polyfulvene

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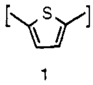
Contribution No. 7666 from the Arnold and Mabel Laboratory of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125. *Received September 17, 1987*

Abstract: At the level of Hückel theory, polyfulvene (PF) has a valence band/conduction band degeneracy much like that seen in polyacetylene. Higher levels of theory remove the degeneracy, but the band gap (E_g) is predicted to be significantly smaller than analogous structures such as polythiophene and polypyrrole at a fulvenoid geometry. An alternative geometry, which we have termed quinoid, is also conceivable for PF, and it is predicted to have a much larger E_g. The effects of benzannelation to produce analogues of polyisothianaphthene (3) have been evaluated. We propose a new model for such structures based on conventional orbital-mixing arguments. Several of the proposed structures have quite interesting properties, which suggest that they are excellent candidates for conducting polymers.

Since the discovery that polyacetylene can be doped to yield highly conducting materials, the number of conducting organic polymers has been increasing steadily.[1] Among the most studied of these compounds are those based on five-membered aromatic rings, such as polythiophene (**1**), polypyrrole (**2**), and related structures. Recently, the benzannelated derivative polyisothianaphthene (**3**) has been prepared and found to have quite intriguing and potentially useful properties,[2] including the fact that it appears to be a transparent conductor. These findings prompted further theoretical work on such ring systems.[3,4,20]



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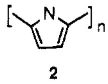

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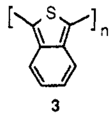

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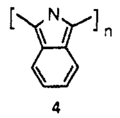

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Polyfulvene (PF) is a nonaromatic, hydrocarbon analogue of polypyrrole and polythiophene. It may also be viewed as a nonalternant isomer of poly-*p*-phenylene. In this paper we present

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(1) Frommer, J. E.; Chance, R. R. In *Encyclopedia of Polymer Science and Engineering*; Grayson, M., Kroschwitz, J., Eds.; Wiley: New York, 1985. Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361–381.

(2) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382–3384. Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717–5723. Colaneri, N.; Kobayashi, M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1986**, *14*, 45–52.

(3) Brēdas, J. L.; Themans, B.; Andrē, J. M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *11*, 343–352.

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