3234 *J. Am. Chem. Soc.* **1987**, *109*, 3234–3240

Nature of Conjugation in Hydronitrogens and Fluoronitrogens. Excessive Flow of Unshared Electron Pairs into σ-Bonds

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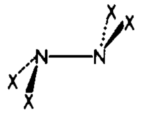
Abstract: A conceptually useful approach to understanding the interbond interactions is described in terms of bond-to-bond delocalization of electrons. The theoretical method has been applied to the analysis of the electron distribution in some linear and cyclic conjugated hydronitrogens (N_mH_n) and fluoronitrogens (N_mF_n) of which only a few are known. The bonding between the N═N bonds in tetrazadiene and fluoro derivative **3** is extremely weak due to the excessive flow of the geminal as well as vicinal unshared electron pairs into the antibonding σ^*-orbital. The same effect similarly weakens the σ-bonds in cyclic conjugated hydronitrogens and fluoronitrogens, i.e., hexazine **6** and pentazoles **7**. The bonding between the N═N bond and the NH_2 group in triazene **4** and 2-tetrazene **5** is relatively strong due to the π-conjugation between the p lone pair of electrons and the double bond. New light is shed on the bonding in isoelectronic nitrogen oxides (N_mO_n), hydrophosphorus (P_mH_n), mixed analogues ($P_lN_mH_n$), and phosphazenes.

Nitrogen can, in principle, constitute molecules which are isoelectronic to the corresponding carbon compounds. However, the chemistry of hydronitrogens (N_mH_n) has been much less advanced than that of hydrocarbons (C_mH_n). Only a few hydronitrogens are known as familiar species. Among them are molecular nitrogen (N_2), ammonia (NH_3), hydrazine (**1**; X = H), and diazene or diimide (**2**; X = H). These molecules have no or one N–N bond.

Of simple higher hydronitrogens (**3**–**7**; X = H), those isolated so far[1] are hydrogen azide or hydrazoic acid (HN_3)[2] and 2-tetrazene (**5**; X = H).[3] The other hydronitrogens described in the literature have been postulated as reaction intermediates or detected by spectroscopic methods under extreme conditions. Tetrazadiene (**3**; X = H) has been postulated as an intermediate in the photolysis of hydrogen azide (HN_3) in Ar, CO, and N_2 matrices.[4] Hexazine **6** was recently suggested to be a product of photochemical reductive cis elimination of *cis*-diazidobis(triphenylphosphine)platinum(II) in solution at 77 K.[5] The parent molecule of triazene (**4**; X = H) has never been isolated while many derivatives with organic substituents are known.[1] Although pentazole (**7**; X = H) has not been prepared as yet, the phenyl derivative, first deduced from the kinetic experiment to be present in solution,[6] has been isolated and characterized.[7] For saturated hydronitrogens, triazane (NH_2NHNH_2)[8] can be isolated as $N_3H_5 \cdot H_2SO_4$, and tetrazane ($NH_2NHNHNH_2$)[9] was postulated to be generated by the dimerization of hydrazyl radicals.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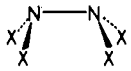
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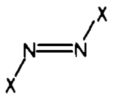
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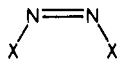
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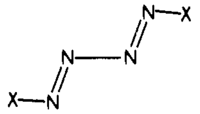
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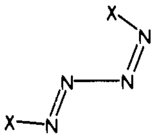
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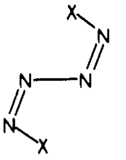
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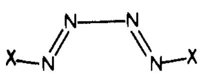
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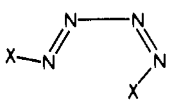
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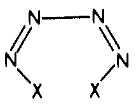
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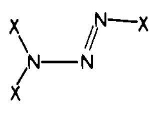
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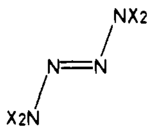
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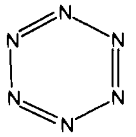
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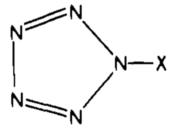
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The chemistry of fluoronitrogens (N_mF_n) has similarly made less progress. The species isolated so far are trifluoroammonia (NF_3), difluorodiazene (**2**; X = F), and tetrafluorohydrazine (**1**; X = F). Tetrafluorohydrazine[10] is often employed to investigate the equilibrium with NF_2 induced by IR laser. Difluorodiazene[11] has been synthesized from NF_2NF_2 or NF_3, and the thermodynamic parameters of reversible cis–trans isomerization were determined.[12] In the reaction of ammonia with fluorine, NF_3, N_2F_4, and N_2F_2 have been detected by NMR and mass spectroscopy.[13] To our best knowledge, there are, however, no reports about the higher fluoronitrogens with two or more N–N bonds.

Although the number of known hydronitrogens is small, each molecule has unique and useful properties. For example, hydrazines (**1**; X = H) and diazenes (**2**; X = H) have been widely used to reduce unsaturated functional groups in organic mole-

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cules.[14] The organic derivatives of triazene (**4**; X = H)[15] have been well established to have antitumor activity against Sarcoma-180 and L1210 leukemia in mice. These facts suggest that unknown hydronitrogens may also be of potential utilities.

At the present stage there are many questions on chemical and physical properties of hydro- and fluoronitrogens. In order to advance the chemistry of these classes of molecules on well-founded basis, we feel it necessary to understand fundamental nature of chemical bonding between nitrogens. There are some theoretical works[16-25] on the higher hydronitrogens. Most of them[16-22] have been undertaken to investigate the aromaticity of cyclic conjugated hydronitrogens. For fluoronitrogens, no theoretical papers have been reported about those with two or more N–N bonds while there are some about the lower homologues.[26]

In this paper we report our theoretical study of the bonding in π-conjugated hydro- and fluoronitrogens. Tetrazadiene (**3**; X = H) is employed as a model compound for acyclic conjugated systems. A cyclic model is hexazine **6**. Triazene (**4**; X = H) and 2-tetrazene (**5**; X = H) are used to investigate the bonding between amino (NH_2) nitrogens and N=N bonds. A cyclic model is pentazole (**7**; X = H). The fluoronitrogens of the present interest are difluorodiazene (**2**; X = F), difluorotetraazadiene (**3**; X = F), and fluoropentazole (**7**; X = F).

Theoretical Background and Method of Calculation. The molecule-in-molecule approach[27] helps us understand the electronic structures of molecules. The wavefunctions are expressed by a linear combination of electron configurations based on orbitals of component subsystems. The first configuration, Φ_G, is termed

$$\Psi = C_G\Phi_G + C_T\Phi_T + C_E\Phi_E \qquad (1)$$

the ground configuration where neither electron shift between any pair of subsystems nor electron promotion in any subsystems take place. The second configuration, Φ_T, is the electron-transferred configuration where an electron is shifted from an occupied orbital of a subsystem to a vacant orbital to another. The third is the locally excited configuration, Φ_E, where an electron is promoted from an occupied to a vacant orbital in a subsystem. The method of configuration analysis[28] is a mathematical procedure to give coefficients (C_G, C_T, and C_E) of electron configuration by expanding the Slater determinants for the electronic structure of the whole system.

The molecule-in-molecule method or the configuration analysis was recently shown to be useful and powerful in understanding electronic structures of molecules in terms of *chemical bonds*.[29-32] In these cases, each subsystem is a chemical bond. The transferred configurations stand for the bond-to-bond delocalization of electrons. The locally excited configurations stand for the bond polarization.

The magnitude of the configuration coefficients, C, provides us with the information about the details of the electronic structure or about the contribution of the configurations. When we compared the corresponding parts of the electronic structure in different molecules, we were encountered with a problem. The number of configurations increases with the size of molecules or with the number of subsystems. The magnitude of coefficients, relatively, decreases because of the normalization even if the chemical situation is equivalent. Therefore, we employ the coefficient ratio to the ground configuration, $C_{T(E)}/C_G$, as a preferable measure rather than $C_{T(E)}$ itself. The rigorous meaning was presented in our previous paper.[31]

Nature of bonding is closely related to the electron population, which is given by the integration of the square of eq 1 all over the space followed by multiplication by the total number of electrons, N

$$N = N\sum_{I} C_I^2\langle I|I\rangle + 2N\sum_{I>J} C_I C_J\langle I|J\rangle \qquad (2)$$

where I and J are electron configurations. The predominant configuration is the ground configuration. The largest of the first terms is then the contribution from it. The integral of the square of the ground configuration can be expanded by using the overlap integral $\langle i|j\rangle$ of the occupied orbitals, i and j, of different subsystems.

$$\langle G|G\rangle = 1 - \sum_{i>j}\langle i|j\rangle^2 + \text{(higher order terms)} \qquad (3)$$

The unity corresponds to the electron distribution of the hypothetical state where each bonding or nonbonding orbital is occupied by a pair of electrons without overlapping. The second terms are the corrections due to the overlap between the occupied orbitals. They are always of negative values. The overlapping repels electrons from the region where the occupied orbitals interact with each other. The interacton is then antibonding, and usually termed exchange repulsion. We define a quantity, exchange population (ExP), to estimate the effect.

$$\mathrm{ExP}(i,j) = -NC_G^2\langle i|j\rangle^2 \qquad (4)$$

The exchange population increases with the overlapping between the occupied orbitals to reduce the bonding property as is readily seen in the definition. The population is also dependent on the magnitude of the coefficient (C_G) of the ground configuration. As electrons localize well, the contribution of the ground configuration is large. The exchange population then increases with the electron localization.

The most important in the second terms of eq 2 is associated to the interactions between the ground and transferred configurations. The interactions contribute most to bonding between the subsystems due to electron delocalization. We here propose a quantity, delocalization population (DP), as a measure of bonding

$$\mathrm{DP}(i\text{–}j^*) = 2NC_G C_{T(i\text{–}j^*)}\langle G|T(i\text{–}j^*)\rangle \qquad (5)$$

where i and j* denote the occupied and vacant orbitals of different subsystems involved in the electron shift. The delocalization

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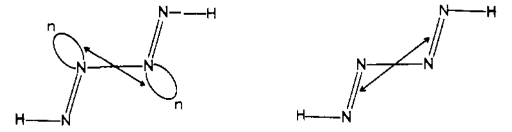
Chart I



$ExP(n,n) = -0.205$ [r(N-N)=1.50Å]
$= -0.263$ [r(N-N)=1.45Å]
$\Delta = 0.058$

$ExP(\sigma_{NN},\sigma_{NN}) = -0.055$ [r(N-N)=1.50Å]
$= -0.069$ [r(N-N)=1.45Å]
$\Delta = 0.014$

(a) (b)

population increases as the occupied orbitals overlap with the vacant orbitals. As electrons delocalize, the contribution of the transferred configurations is large.

The delocalization population defined above comes from the direct interaction between the occupied and vacant orbitals or between the ground and transferred configurations. The delocalization appreciably occurs where the occupied and vacant orbitals are close to each other or between the adjacent bonds. However, farther delocalization is important in long or cyclic conjugated systems. This delocalization is described in terms of the interaction between the transferred configurations,[29-32] which is contained in the second terms of eq 2. The delocalization population (DP) is defined here as follows

$$\mathrm{DP}(\mathrm{i-j^*}|\mathrm{i-k^*}) = 2NC_{\mathrm{T(i-j^*)}}C_{\mathrm{T(i-k^*)}}\langle \mathrm{T(i-j^*)}|\mathrm{T(i-k^*)}\rangle \quad (6)$$

$$\mathrm{DP}(\mathrm{i-j^*}|\mathrm{k-j^*}) = 2NC_{\mathrm{T(i-j^*)}}C_{\mathrm{T(k-j^*)}}\langle \mathrm{T(i-j^*)}|\mathrm{T(k-j^*)}\rangle \quad (7)$$

In the present work each subsystem is taken to be a chemical bond or an unshared electron pair. The orbitals treated here are the bond orbitals and the nonbonding orbitals. The nonbonding orbitals are simply the atomic or hybrid orbitals. The bonding and antibonding orbitals are the in-phase and out-of-phase combinations of them, respectively.

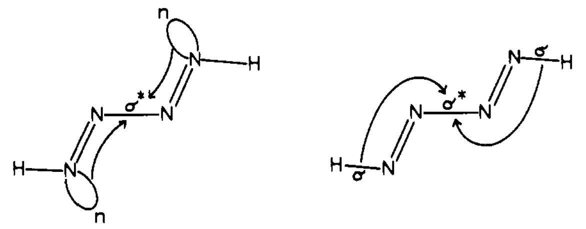
Molecular geometries of the model compounds have never been determined by experiments. We have optimized the geometries by ab initio molecular orbital calculations. The experimental value for the N=N bond in *trans*-diazene is 1.252 Å.[33] The length optimized with the STO-3G basis sets[34] is 1.267 Å, in fairly good agreement, compared with those with the other basis sets (6-21G, 1.240 Å; 3-21G, 1.239 Å; 4-31G, 1.226 Å).[34] The experimental value for the N–N bond in hydrazine is 1.446–1.449 Å.[35] The STO-3G optimized length (1.459 Å) is rather close to the experimental value and to the 6-31G* (CI) optimized length (1.448 Å)[36] than those with 4-31G (1.399 Å) and 4-31G* (1.414 Å) basis sets.[36] In view of these literature values and economic reason the STO-3G basis set is of our choice.

Results and Discussion

Tetrazadiene. The optimized bond lengths of the hydronitrogens are listed in Table I. The lengths of the N=N bonds in tetrazadienes are almost unchanged on conjugation except for sterically congested s-cis-*E*,*Z* and *Z*,*Z* isomers (**3e**, **3f**; X = H). The deviation from the N=N bond length of diazenes is negligibly small (0.003 Å) for each of the *E* and *Z* conformations. The N=N bonds in **3e** and **3f** are a little shorter.

The N–N single bonds (~1.50 Å) of the tetrazadienes (**3a**–**3d**; X = H) are surprisingly long for the standard atomic distance (1.45 Å)[37] between singly bonded nitrogen atoms. These bonds are longer than those (~1.48 Å) in cis and trans conformations of hydrazine (**1**; X = H). The N–N bond lengths are still longer than the optimized C–C bond in butadiene (1.488 Å). The sterically crowded conformers (**3e**, **3f**; X = H) have an incredibly long "bond". The anomaly suggests the instability of the tetrazadienes.

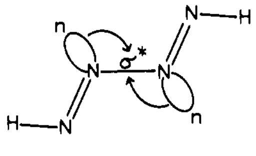
Chart II



$C_{n\to\sigma^*_{NN}}/C_G = 0.064$[r(N-N)=1.50Å]
$= 0.055$[r(N-N)=1.45Å]
$\Delta = 0.009$

$C_{\sigma_{NH}\to\sigma^*_{NN}}/C_G = 0.080$ [r(N-N)=1.50Å]
$= 0.073$ [r(N-N)=1.45Å]
$\Delta = 0.007$

(a) (b)



$C_{n\to\sigma^*_{NN}}/C_G = 0.297$ [r(N-N)=1.50Å]
$= 0.272$[r(N-N)=1.45Å]
$\Delta = 0.025$

(c)

Chart III

$C_{n\to\sigma^*_{NN}}/C_G = 0.183$
$= 0.258$[r(N-N)=1.45Å]

$C_{n\to\sigma^*_{NN}}/C_G = 0.110$ [r(N-N)=1.45Å]

In order to look into the unusual property of the tetrazadienes, the structure of the optimized geometry was compared with that of the standard N–N bond length (1.45 Å). The electronic structures were subjected to the configuration analysis. The exchange and delocalization populations (ExP and DP) and the coefficient ratio (C_T/C_G) were calculated for the most stable s-trans-*E*,*E* conformer.

Although tetrazadiene can be stabilized by lengthening the N–N bond to avoid the exchange repulsion between the nonbonding orbitals on the inner nitrogen atoms (Chart Ia), the repulsion is not considered to be a primary factor of the abnormal bond length. On shortening the N–N single bond from 1.50 to 1.45 Å, the exchange population changes more significantly (−0.058) than that (−0.014) for the σ_{NN}–σ_{NN} interaction (Chart Ib). However, the n–n repulsion (−0.263) is still smaller than that (−0.299) in hydrazine which has a stable N–N bond.

The N–N single bond in tetrazadiene may be weakened by electron inflow from the surrounding bonds and lone pairs of electrons of high electron-donating power. We estimated the effects by the coefficient ratio (C_T/C_G) of the transferred configurations. The outstanding electron inflow was found to occur from the lone pairs of electrons on the inner nitrogen atoms (0.297), which are geminal to the N–N single bond (Chart IIc). The inflow from the vicinal entities on the outer nitrogens is also

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Table I. Bond Lengths[a] (Å)

compd	N=N (1.252[b])		N-N (1.447[c])		
	E	Z	s-trans	s-cis	N-N
1a (X = H)			1.481		
1b (X = H)				1.483	
2a (X = H)	1.266				
2b (X = H)		1.264			
3a (X = H)	1.269		1.501		
3b (X = H)	1.267	1.263	1.504		
3c (X = H)		1.261	1.507		
3d (X = H)	1.267			1.507	
3e (X = H)	1.260	1.256		1.542	
3f (X = H)		1.249		1.571	
4 (X = H)	1.277				1.388
5 (X = H)	1.280				1.404
6 (X = H)		1.356			
7 (X = H)		1.311		1.412	1.373
2a (X = F)	1.283				
2b (X = F)		1.277			
3a (X = F)	1.280		1.480		
3b (X = F)	1.279	1.273	1.489		
3c (X = F)		1.272	1.495		
7 (X = F)		1.314		1.413	1.382

[a] The STO-3G results. [b] Experimental for diazene.[33] [c] Experimental for hydrazine.[35]

appreciable: 0.064 for the unshared electron pairs (Chart IIa) and 0.080 for the N-H bonds (Chart IIb). Furthermore, these terms were found to be more dependent on the N-N bond length than others. The present calculations and analyses indicated that the geminal and/or vicinal inflow might be most responsible for the unusual weakening of the N-N single bond in tetrazadiene.

The N=N double bonds in diazene as well as tetrazadiene do not suffer from the similar destabilization (Chart III). The antibonding orbital of the σ-bond between the doubly bonded nitrogens lies at a higher energy level because of the stronger interactions of the hybrid orbitals due to the shorter distance. The electron flow into the σ-bond is depressed by the greater energy difference from the electron-donating orbitals. The σ-bond remains intact. In fact, the geminal inflow from the unshared electron pairs in diazene (0.183) is much smaller than that into the N-N single bond in the tetrazadiene (0.272) of the standard N-N bond length. However, the electron flow in diazene increases with the N=N distance or with the σ_{NN^*} energy lowering to be comparable (0.258) to the latter, when the distance is equal to 1.45 Å. These results suggest that the σ-bond between the doubly bonded nitrogen atoms is not significantly weakened by the flow of the geminal lone pair of electrons due to the high-lying σ_{NN^*} orbital.

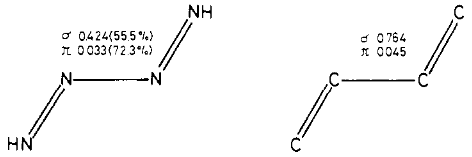
The stability of the N-N bond in hydrazine relative to the N-N single bond in tetrazadiene may be ascribed to the low geminal inflow of electrons (0.110) (Chart III). The electron flow is influenced by the resonance integrals between the n-orbital and the σ_{NN^*}-orbital. The interaction between the sp^3 hybrid orbitals on the same atom is weaker than that between the sp^2 ones due to the small s-character. The sp^3 hybridization depresses the geminal inflow in hydrazine.

We have compared the in-plane bonding between the inner nitrogens in tetrazadiene with that in hydrazine and diazene. Now, we can propose that the geminal flow of electrons especially diminishing the σ-bonding is that from the *sp*^{2} lone pairs of electrons into the *single* bond (Chart IIc).

The π-electrons cannot be considered to be a primary factor of the abnormal N-N single bond lengths in tetrazadiene. The shortening of the N-N bond from the optimized to the standard value increases the π-π exchange repulsion and the π-π^* delocalization attraction, as is expected. The change (0.164 = 0.082 × 2) in the delocalization population is greater than that (−0.068) in the exchange population. The net π-bonding is reduced at the optimized geometry. Tetrazadiene is not considered to gain π-electronic stabilization by lengthening the N-N bond.

The preceding results and discussion lead to a conclusion that the middle N-N bond in tetrazadiene is unusually weak due to σ-electrons. This is supported by the atomic bond population (Chart IV). While the atomic π-bond population in the tetrazadiene of the standard N-N bond length amounts to 72.3% of that in butadiene, the σ component amounts to 55.5%. These values show that the σ-bonding is much more diminished than the π-bonding.

Chart IV



Triazene and 2-Tetrazene. We have seen that the bond between the N=N bonds is extremely weak. We turn our attention to the bond between the N=N bond and the amino group (NH$_2$). The optimized N-N single bond in triazene (1.388 Å) or 2-tetrazene (1.404 Å) is shorter than that in hydrazine. The double bond in triazene (1.277 Å) or 2-tetrazene (1.288 Å) is longer than that in the diazenes (1.264–1.266 Å). These results show that the π-conjugation or the bonding between the N=N bond and the NH$_2$ group is appreciable.[38]

The favorable π-conjugation between the N=N bond and NH$_2$ group relative to that between the N=N bonds is readily understood in terms of the qualitative orbital interaction theory. The electron-donating orbital in triazene is the n-orbital on the amino nitrogen, which lies at a higher energy level than the π-bonding orbital in tetrazadiene. The accepting orbitals are the same for both molecules. The energy separation between the donating and accepting orbitals is smaller in triazene and 2-tetrazene. Furthermore, the n-orbital localizes more than the π-orbital and overlaps with the accepting π^*-orbital to a greater extent. It follows that the orbital interaction for the electron delocalization is predicted from the orbital energy gap and overlapping to be greater in triazene and 2-tetrazene than in tetrazadiene. The results of the calculations confirmed the prediction. The delocalization population is 1.264 in triazene and 1.107 in 2-tetrazene, while 0.734 (= 0.367 × 2) in the tetrazadiene of the standard N-N bond length.

The appreciable π-bonding between the N=N bonds and the NH$_2$ groups is supported even if the exchange repulsion is taken into account. The overlapping between the occupied π-orbitals is greater in triazene and 2-tetrazene, as is similarly expected. The exchange population is −0.512 in triazene and −0.631 in 2-tetrazene while −0.304 in the tetrazadiene of the standard bond length. The net bonding properties, indicated by the difference between the delocalization and exchange populations, show that the π-bonding is outstanding in triazene (0.722) and a little greater in 2-tetrazene (0.476) than in tetrazadiene (0.430).

The preceding results of the calculations incidentally revealed that the magnitudes of the π-bonding between the N=N bond and the NH$_2$ groups in triazene and 2-tetrazene are considerably different from each other. This is substantiated by the ^{1}H NMR spectroscopy.[39] The barrier for rotation about the N-N single bond is lower in the 2-tetrazene derivatives (**5**; X = SiMe$_3$, GeMe$_3$, SnMe$_3$) than in the silyl derivative of triazene **4**. This can be understood in terms of cyclic orbital interaction in acyclic conjugation, a new concept developed recently.[30] The delocalization of six π-electrons in linear conjugated four p-orbital systems such as 2-tetrazene is depressed by the orbital phase discontinuity, while a similar phase restriction is absent in triazene.

Triazene and 2-tetrazene have sp^2 lone pair(s) of electrons geminal to the N-N single bond(s) and vicinal electron-donating groups (Chart V), which have been proposed to destabilize the N-N bond in tetrazadiene. However, the destabilizing entities are absent on a side of the N-N bond or on the NH$_2$ group in triazene and 2-tetrazene, while present on both sides in tetraza-

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(38) Triazene has been studied with use of ab initio molecular orbital calculations[25] [3-21G, r(N-N) = 1.360 Å r(N=N) = 1.243 Å; 6-31G, r(N-N) = 1.326 Å and r(N=N) = 1.235 Å].

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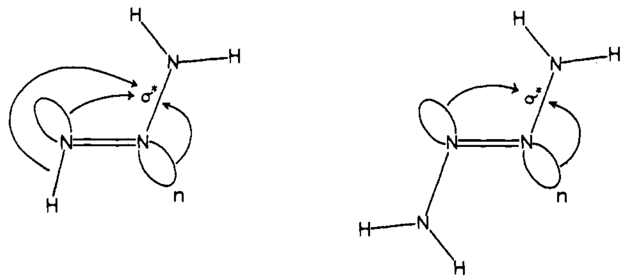
Chart V



diene. We speculate that the stability of the N–N bond between the N═N bond and the NH_2 group relative to that between the N═N bonds is, at least partially, attributed to the absence of the geminal/vicinal electron flow from the NH_2 group.

Pentazole and Hexazine. The effects of π-conjugation were found in the optimized geometries of pentazole (**7**; X = H)[20a] and hexazine (**6**; X = H). The N═N bond in pentazole is 0.05 Å longer than that in diazene. The N–N bond in the tetrazadiene moiety of pentazole is 0.07 Å shorter than that in hydrazine. The bond length (1.356 Å) in hexazine is nearly intermediate between those in hydrazine and diazene. No evidence for the instabilities of the cyclic conjugated hydronitrogens suggested by the experimental[5] and theoretical[10] works was found in the optimized geometries of the cyclic conjugated hydronitrogens. More sophisticated ab initio molecular calculations recently gave controversial results about hexazine. The DZ basis set yielded the prediction that the equilibrium geometry of hexazine is of D_{3h} structure [r_1(N═N) = 1.295 Å, r_2(N═N) = 1.353 Å],[22] the D_{6h} structure being a transition state.[20] Contrary to this, the D_{6h} hexazine [r = 1.288 Å] is an energy minimum at a DZ + P level.[22]

For cyclic delocalization of π-electrons the interactions between transferred configurations are important in addition to those between the ground and transferred configurations.[29,31] The latter, estimated by DP(G|T) in eq 5, represents the delocalization to the neighboring bonds. The interaction does not involve farther delocalization required for cyclic delocalization. The interactions between the transferred configurations, estimated by DP(T_i|T_j) in eq 6 and 7, are indispensable for cyclic delocalization. In this sense, DP(G|T) is tentatively termed *acyclic* delocalization population, the DP(T_i|T_j) being termed *cyclic* delocalization population.

The acyclic π-delocalization population between the double bonds is higher in pentazole (0.781) and hexazine (0.857) than that in tetrazadiene (0.571). This makes a contrast to the hydrocarbon analogues. The delocalization in benzene (0.959) and pyrrole (1.115) is lower than that of butadiene (1.136). The aromatic character cannot be discussed in this term.[31] The cyclic delocalization population is appreciable in pentazole (0.207) and hexazine (0.259). However, the magnitudes are low relative to pyrrole (0.261) and benzene (0.284). The aromaticity of the hydronitrogens is insignificant relative to the isoelectronic hydrocarbons.

The in-plane electronic structures were then scrutinized. The exchange population between the unshared electron pairs in pentazole and hexazine is comparable with that between the C–H bonds in pyrrole and benzene (Chart VI). For example, the exchange population between the n-orbitals on the doubly bonded nitrogens in pentazole and that between the corresponding C–H bonds in pyrrole are of almost the same values (−0.097). The population (−0.069) between the unshared electron pairs on the singly bonded nitrogens in pentazole is close to that (−0.079) between the corresponding C–H bonds in pyrrole. This is also the case with hexazine (−0.110) and benzene (−0.129). These results show that the n–n repulsion makes no appreciable difference from the hydrocarbon counterparts.

The flow of the lone pairs of electrons into the N–N single bonds destabilizes the cyclic conjugated hydronitrogens as much as the acyclic ones, as is shown by the coefficient ratios of the transferred configurations (Chart VII). The geminal inflow in hexazine (0.211) or pentazole (0.262) is greater than that in hydrazine (0.110) or diazene (0.183). The vicinal inflow in hexazine (0.101) or pentazole (0.129) is far greater than that (0.064) in tetrazadiene.

Chart VI

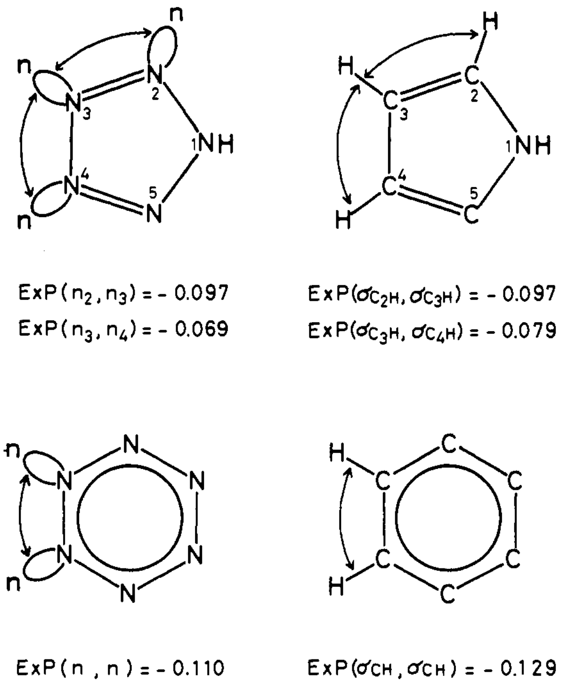
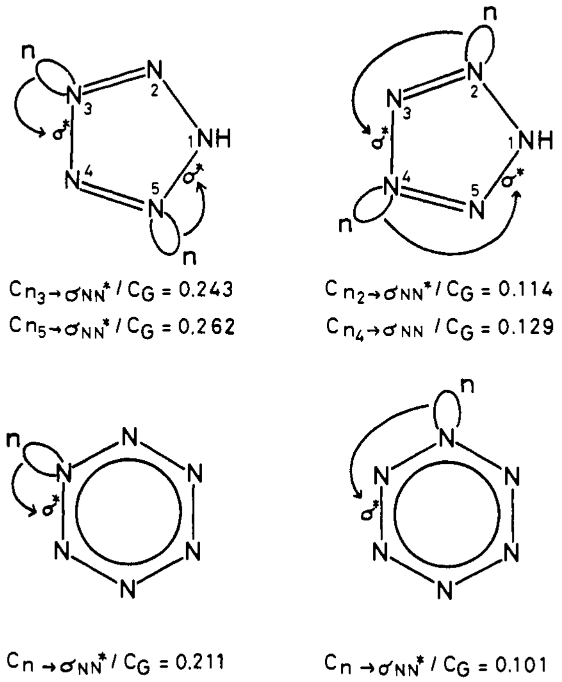


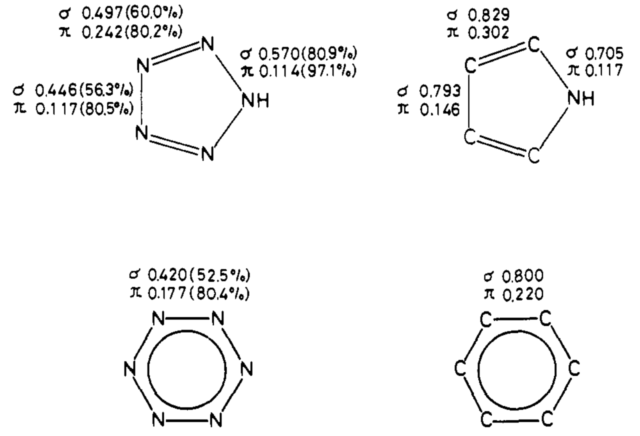
Chart VII



We can see the effects of the σ and π electrons in the atomic bond population (Chart VIII). The π component of the atomic bond population in the cyclic hydronitrogens amounts to 80% of that in the reference hydrocarbons while the σ component amounts to 50%–60%, except for the triazene conjugation in pentazole. These values show that the in-plane bonding is significantly weaker in the hydronitrogens. As a result, the most destabilizing factor of cyclic conjugated hydronitrogens may be concluded to be also the excessive flow of the unshared electron pairs into the σ-bonds, while the low aromaticity is partially responsible.

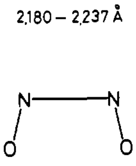
Fluoronitrogens. The optimized bond lengths of the fluoronitrogens (Table I) indicated that they make no considerable difference from the hydronitrogens. The N–N bond lengths in difluorotetrazadienes are similar (~1.50 Å). The calculated

Chart VIII



populations (DP and ExP) and the coefficient ratios $C_{T(E)}/C_G$ of the configurations also confirmed that the electronic features are similar to those of the hydronitrogens.

Nitrogen Oxides. Dinitrogen dioxide **8** is an isoelectronic molecule of tetrazadiene. If the similar effects of the unshared electron pairs are predominant, the N–N bond in dinitrogen dioxide is expected to be weak and long. In fact, the observed bond distances are 2.180 Å in the solid phase[40] and 2.237 Å in the gas phase.[41] The dissociation energy is 1.6 kcal/mol.[42]



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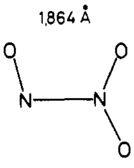

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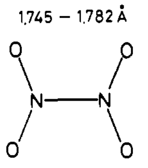

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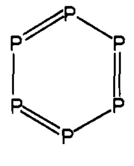
Support for the importance of the geminal flow of electrons is given by the order of the N–N bond lengths of the nitrogen oxides. In dinitrogen trioxide **9** and dinitrogen tetroxide **10** one or two geminal sp^2 lone pairs of electrons are replaced by the electron-withdrawing NO bond(s). If the geminal delocalization is predominant, the N–N bond length should decrease in the order of **8** > **9** > **10**. This is confirmed by the observed values, i.e., 1.864 Å for **9**[43] and 1.745–1.782 Å[44] for **10**. The still long bond can be accounted for by the increasing number of the vicinal lone pairs of electrons on oxygens.[45]

Hydrophosphorus. The chemistry of hydrophosphorus (P_mH_n) and the mixed analogues ($P_lN_mH_n$), especially higher conjugated compounds, has made much less progress. Very recently, hexaphosphabenzene **11** was prepared and characterized as the central bridge ligand in the triple-decker sandwich Mo complex.[46] The mixed analogue, P_3N_3 **12**, has been detected and found to be unstable.[47] In contrast to these conjugated molecules, phosphazenes **13** and **14** are known as relatively stable molecules, and the polymers **15** are extensively investigated due to the potential utility in the technological fields.[48] The present study gives an interpretation upon the stability of phosphazenes relative to the conjugated compounds. The conjugated molecules have geminal and vicinal sp^2 lone pairs of electrons on both sides of each N–N, N–P, or P–P bond. This is the critical factor proposed to destabilize the bond. The unfavorable condition is absent in phosphazenes where the lone pairs of electrons on phosphorus are replaced by the electron-withdrawing σ-bonds such as P–O and P–N.



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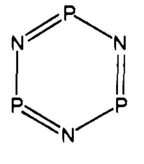

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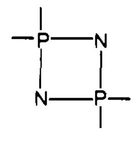

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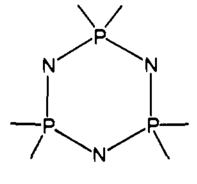

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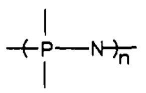

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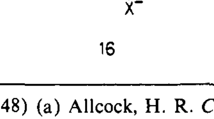
2,3-Diazabutadiene. Although the N–N bond length (1.418 Å) determined by the electron diffraction study[49] is shorter than in hydrazine (1.447 Å), the shortening (0.03 Å) on conjugation is substantially less than that (0.07 Å) found for butadiene. It is likely that the electron inflow of the geminal unshared electron pairs prevents the N–N bond from shortening.

Conclusions

We theoretically investigated the geometrical and electronic structures of some conjugated N_mH_n and N_mF_n. The ab initio molecular orbital calculations with STO-3G basis sets showed a surprising geometrical feature of unknown tetrazadiene **3**, a model for the bonding between the N=N bonds in the linear conjugated hydronitrogens. The N–N bond is extremely weak and long, while the optimized bond lengths in hydrazine **1**, diazene **2**, triazene **4**, and 2-tetrazene **5** are in fairly good agreement with the experimental observation or at least in the usually expected ordering in spite of the rigid basis functions employed. We have proposed some intrinsic properties which diminish the bonding, i.e., the n–n exchange repulsion (Chart Ia) and the excessive electron flow into the σ*-orbitals from the geminal lone pairs of electrons (Chart IIc) and from the vicinal N–H bond (Chart IIb) and lone pair of electrons (Chart IIa). Predominant is the electron inflow from the surrounding electron-donating entities into the N–N bond. In view of the present results and the known properties of N_2O_2, tetrazadiene may exist as an "association" molecule of diazenyl radicals (N=NH). The excessive electron flow also weakens the in-plane or σ-bonding between the nitrogen atoms in cyclic conjugated hydro- and fluoronitrogens, e.g., hexazine, pentazole, and their fluoroderivatives **6** and **7**.

The bonding between the N=N bond and the NH_2 group in triazene **4** and 2-tetrazene **5** is appreciable, as is expected from the π-conjugation. It should be noted also that these molecules have, on the NH_2 group, neither in-plane sp^2 unshared electron pairs nor the N–H bond vicinal to the N–N single bond.

The present work suggests two strategies for preparing "stable" hydronitrogens and fluoronitrogens. Substituents (see **16**) should



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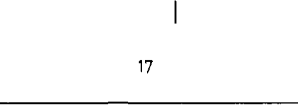

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be introduced in order to keep the lone pairs of electrons from flowing into the σ^*-orbital. As many linkages between the amino nitrogens and N=N bonds in **17** should be contained as possible.

Acknowledgment. The ab initio molecular orbital calculations were carried out on a HITAC-M200H computer, Institute for Molecular Science, with the IMSPAK program. The subsequent configuration analysis was carried out on a FACOM M-360 computer, Gifu University Computing Center. This work was partially supported by Saneyoshi Scholarship Foundation.

Electronic and Steric Factors Determining the Asymmetric Epoxidation of Allylic Alcohols by Titanium–Tartrate Complexes (The Sharpless Epoxidation)

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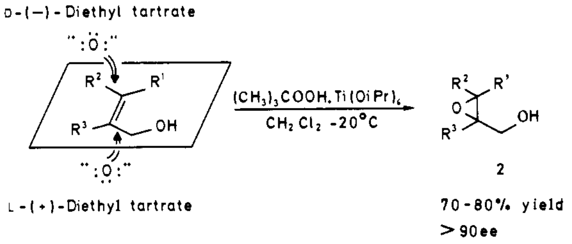
Received August 25, 1986

Abstract: The structure and epoxidation properties of titanium–tartrate asymmetric epoxidation catalysts have been studied by using the frontier orbital approach. It is suggested that an important factor determining the dimeric structure of these titanium–tartrate epoxidation catalysts is electronic, as one of the LUMOs, located at the titanium atom, is oriented so it facilitates nucleophilic trans coordination to the titanium of the carbonyl group in the tartrate. Coordination of a peroxide to titanium–tartrate is analyzed. From the frontier orbitals at the equatorial peroxygen, four possible orientations of the allylic alcohol are possible. Analysis of the preferred orientation of a hydroxyl and a methoxy group at the equatorial site at the titanium atom, and of an alkene around the peroxygen, led to a spiro orientation of the alkene part of the allylic alcohol at the peroxygen as the most probable. The preferred orientation of the allylic alcohol at the titanium atom is discussed in relation to electronic as well as steric interactions with the tartrate. The orientation and reactivity of the alkene part of the allylic alcohol can be traced to two two-electron interactions: one is the peroxygen lone pair electron interaction with the π^* orbital of the alkene part of the allylic alcohol and the other is the interaction of the titanium–peroxygen antibonding orbital with the π orbital of the alkene.

Epoxidation of alkenes, and especially asymmetric epoxidation, is a fundamental and important organic reaction type. The asymmetric epoxidation was pioneered by Herbst, who used chiral monoperoxycamphoric acid to produce chiral epoxides with an enantiomeric excess of 5% or less;[1] later Pirkle and Rinaldi were able to improve the enantiomeric excess to 9%.[2] Catalytic epoxidation with hydrogen peroxide and *tert*-butyl hydrogen peroxide catalyzed by chiral phase-transfer agents such as benzyl guinidinium salts was investigated by Hummelen and Wynberg, with moderate success.[3] The first transition metal catalyzed asymmetric epoxidation was reported independently by Sharpless et al.[4] and Yamada et al.,[5] the first with vanadium and the second molybdenum complexes. Further examples of molybdenum-catalyzed epoxidations were reported by Otsuka et al.,[6] who described the treatment of squalene with a mixture of *tert*-butyl hydroperoxide, chelated molybdenum oxide, and the chiral inducing agent (+)-diisopropyl tartrate. By this method it was possible to obtain (*S*)-2,3-squalene epoxide in 14% enantiomeric excess.

The real breakthrough in asymmetric epoxidation came when Sharpless et al. treated a mixture of commercially available titanium tetraisoproxide, *tert*-butyl hydroperoxide, and (+)- or (−)-diethyl tartrate with allylic alcohols.[7] With (−)-diethyl tartrate the oxidant approaches the allylic alcohol from the top side of the plane shown in **1**, whereas the bottom side is open for the (+)-diethyl tartrate reagent, giving rise to the corresponding optically active epoxy alcohols, **2**. This asymmetric epoxidation, now known as the Sharpless epoxidation, has already shown its power in the synthesis of natural products.[8]



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Recently the structures of a series of titanium–tartrate derivatives have been published,[7h,i,9] and two of these structures are

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