

between the calculated and experimental frequencies varies somewhat, indicating that better agreement might be obtained by using somewhat different scaling factors for CH and CC force constants, for example. In the CCl and CS stretching frequency region (790–690 cm^{-1} in the experimental spectrum) the calculation is not in very good agreement with experiment, as expected. Furthermore, the heavy atom (S and Cl) involvement in the low-wavenumber region (in general below 790 cm^{-1}) introduces considerable error in our calculated spectrum in this region. In spite of these problems, the general agreement between the calculated spectrum and the experimental spectrum, even for this very complicated molecule, is encouraging.

We shall not discuss further here the experimental spectra of these compounds^{16a} and the use of our calculated spectra for their assignment, since a detailed analysis of this problem will be the subject of later papers. However, we should point out that the comparison (given above) of our calculated spectra with previous experimental studies leads us to expect that the predicted spectrum will be in very good agreement with the experimental spectrum for the isolated, all-trans conformers of these molecules *except*

for the values predicted for the C–S, S–H, and C–Cl stretching frequencies, using the 0.89 scaling factor. The comparison between the spectra calculated for the two $\text{CH}_3\text{CH}_2\text{SH}$ conformers indicates how the conformational changes will affect the predicted spectra, and we shall discuss this subject in more detail elsewhere.^{16b}

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Computational Determination of the Structures and Some Properties of Tetrahedrane, Prismane, and Some of Their Aza Analogues

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We have carried out an ab initio self-consistent field computational study of tetrahedrane, prismane, and nine of their aza analogues, in which C–H units have been replaced by nitrogens. Structures optimized at the 3-21G level were used to compute molecular electrostatic potentials, as guides to reactive behavior, and bond deviation indexes as quantitative indicators of bond strain. Within each set of azaprismane isomers, the most stable is the one having the fewest N–N bonds. The exceptional length of these bonds, approximately 1.59 Å, may reflect a tendency to rupture. In the tetrahedranes, the bonds are quite highly strained but become less so as the number of nitrogens increases. The degrees of bond strain are not as great in the prismanes and do not necessarily diminish as more nitrogens are introduced. There are negative electrostatic potentials associated with the C–C bonds in tetrahedrane and prismane, indicating that these bonds can serve as initial sites for electrophilic attack. These potentials are greatly weakened or eliminated by the introduction of nitrogens. In the azatetrahedranes and azaprismanes, there are strong and extensive negative regions near the nitrogens, suggesting significant basicity; these also become weaker as the number of nitrogens increases.

Introduction

Tetrahedrane, I, and prismane, II, are highly strained hydrocarbons, with estimated strain energies of roughly 130 kcal/mol.¹ While molar strain energies higher than this have been attributed to certain other cage-type molecules (e.g., cubane, III, 157 kcal/mol¹), tetrahedrane and prismane are certainly among the very highest on a weight basis or relative to the number of C–C bonds.



This intrinsic instability suggests that the syntheses and isolation of these compounds may be extremely difficult, and indeed tetrahedrane is as yet unknown. However, prismane has been prepared and found to be stable at room temperature;² this may reflect the fact that several of its likely potential transformations are thermally forbidden.^{1,3,4} Since analogous restrictions apply

to tetrahedrane,^{1,4,5} its eventual synthesis remains a realistic possibility; indeed it has been implicated as an intermediate in several different reactions.⁶⁻⁹

Derivatives of both molecules are known. Tetra-*tert*-butyl-tetrahedrane has been prepared,¹⁰ and there have been at least indications of the formation of other substituted tetrahedranes.^{1,11-13} Several alkyl derivatives of prismane have been isolated.^{1,14-16}

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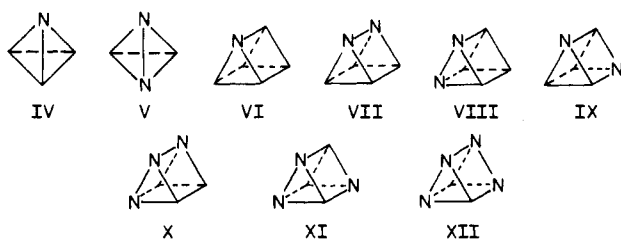
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Our ultimate objectives are to gain insight, by computational methods, into the anticipated stabilities and reactive properties of methyl, amino, and nitro derivatives of (a) tetrahedrane and prismane and (b) their aza analogues IV–XII, in which one or



more C–H units are replaced by nitrogens. In the initial phase of this study, which is being reported here, we focus upon the parent unsubstituted systems, I, II, and IV–XII. We have calculated and shall discuss their structures, the relative stabilities of the isomers, the molecular electrostatic potentials (as guides to reactive behavior), and the bond deviation indexes (as a quantitative means of comparing strained bonds).

Methods

General. We have used the *ab initio* self-consistent field GAUSSIAN 82 procedure¹⁷ to compute the structures of I, II, and IV–XII at the 3-21G level; this is known to be effective for geometry optimizations¹⁸ and in particular has produced good results for strained systems.¹⁹ These structures were used to calculate the molecular electrostatic potentials and bond deviation indexes. These were obtained with STO-5G and STO-6G basis sets, respectively, which we have found to be very satisfactory for one-electron properties.

Electrostatic Potential. The electrostatic potentials $V(\vec{r})$ that is created in the space around a molecule by its nuclei and electrons is given rigorously by

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r}' - \vec{r}|} \quad (1)$$

Z_A is the charge on nucleus A , located at \vec{R}_A . $\rho(\vec{r})$ is the molecular electronic density function, which we compute.

The electrostatic potential is a well-established means for interpreting and predicting reactive behavior.^{20–22} For example, an approaching electrophile is initially attracted to those regions in which $V(\vec{r})$ is negative, where the effects of the molecule's electrons are dominant, and in particular to those points at which $V(\vec{r})$ reaches its most negative values (the local minima). It is important to note that the electrostatic potential is a real physical property, which can be determined experimentally as well as computationally.²²

Bond Deviation Index. The term "bond path" has been used to denote the ridge of maximum electronic density linking two chemically bonded nuclei.²³ While this often lies along the internuclear axis, as in the C–C bonds in cyclohexane and propane, in other instances, as in strained bonds, it is curved.^{23–29} We have

TABLE I: Calculated Structural Parameters, Bond Deviation Indexes, and Electrostatic Potential Minima

molecule	dist, Å	angle, deg	bond dev index	electrostatic potential min, kcal/mol ^a
I	a: 1.489 ^b	aa: 60	a: 0.114	a: -12.9
IV	a: 1.540 b: 1.452	aa: 56 ab: 62 bb: 60	a: 0.105 b: 0.101	N: -60.6
V	a: 1.503 b: 1.410 c: 1.589	ab: 62 ac: 58	a: 0.091 b: 0.087 c: 0.109	N: -48.6
II	a: 1.535 ^c b: 1.570 ^c	aa: 60 ab: 90	a: 0.077 b: 0.031	a: -13.5 b: -4.3
VI	a: 1.542 b: 1.501 c: 1.561 d: 1.562 e: 1.522 f: 1.545	aa: 58 ad: 88 de: 92 ee: 61	a: 0.064 b: 0.068 c: 0.030 d: 0.016 e: 0.076 f: 0.080	N: -86.6 b: -2.0 f: -3.5
VII	a: 1.538 b: 1.506 c: 1.549 d: 1.592	aa: 59 ad: 89	a: 0.063 b: 0.069 c: 0.027 d: 0.0097	N: -75.3
VIII	a: 1.589 b: 1.507 c: 1.551 d: 1.560 e: 1.504 f: 1.530	bb: 64 bc: 93 cf: 87 ff: 59	a: 0.062 b: 0.053 c: 0.028 d: 0.014 e: 0.074 f: 0.079	N: -77.4
IX	a: 1.553 b: 1.489 c: 1.527 d: 1.552 e: 1.552	ab: 60 ae: 91 be: 89	a: 0.067 b: 0.067 c: 0.062 d: 0.015 e: 0.028	N: -76.6
X	a: 1.581 b: 1.506 c: 1.511 d: 1.538 e: 1.589 f: 1.546 g: 1.518 h: 1.548 i: 1.495	bc: 63 cd: 92 bd: 92 cf: 87 be: 89	a: 0.060 b: 0.052 c: 0.053 d: 0.026 e: 0.0087 f: 0.012 g: 0.061 h: 0.066 i: 0.069	N(acf): -66.7 N(abe): -64.4 N(egh): -64.7
XI	a: 1.601 b: 1.493 c: 1.540 d: 1.549 e: 1.473 f: 1.538	ff: 57 fc: 85 cb: 95 bb: 65	a: 0.066 b: 0.052 c: 0.014 d: 0.013 e: 0.066 f: 0.066	N(cff): -65.8 N(abd): -66.5
XII	a: 1.593 b: 1.487 c: 1.500 d: 1.587 e: 1.535	ab: 58 bd: 88 ad: 90	a: 0.065 b: 0.051 c: 0.053 d: 0.0080 e: 0.011	N(ace): -55.0 N(abd): -52.7

^aThe electrostatic potential minima are indicated as being associated either with bonds or with nitrogens. Nonequivalent nitrogens are distinguished by specifying the bonds that they form. ^bThis value is close to the C–C bond length found crystallographically for tetra-*tert*-butyl-tetrahedrane, 1.487 Å¹⁰ and to that computed for tetrahedrane at the 6-31G*/MP2 level, 1.477 Å (Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 865). ^cThese results agree exactly with the 3-21G optimized bond distances reported in ref 19.

introduced the "bond deviation index", λ , as a numerical measure of the degree of this curvature;²⁵ it is defined by

$$\lambda = \left[\frac{1}{N} \sum_i r_i^2 \right]^{1/2} / R \quad (2)$$

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The r_i are the lengths of N equally spaced lines drawn between the actual bond path and the reference path defined by the superposed electronic densities of the corresponding free atoms placed at the same positions as they occupy in the molecule. We set N to 320, which is well beyond the point at which further increases in its magnitude produce no significant change in λ . R is the internuclear distance; its inclusion permits us to compare λ values for bonds of different lengths.

The bond deviation index provides a means of characterizing and comparing strained chemical bonds.²⁵⁻²⁹ An important feature is that it focuses specifically upon individual bonds, rather than reflecting the molecule as a whole.

Results and Discussion

Structures and Stabilities. Table I lists the key bond lengths and bond angles for molecules I, II, and IV–XII, as obtained by our 3-21G geometry optimizations. For the three tetrahedranes (I, IV, and V), the C–C bonds are shorter and the C–N are longer than their more typical values of about 1.54 and 1.47 Å, respectively.³⁰ Both decrease in length as nitrogens are introduced. Most striking, however, is the exceptionally long N–N bond in V. For comparison, the rather weak N–N bond in hydrazine, N₂H₄, which has a dissociation energy of 58 kcal/mol,³¹ is more than 0.1 Å shorter (1.46 Å³⁰).

Prismane, II, has two different types of C–C bonds, both of which are longer than those in tetrahedrane (Table I). However, the C–N bonds in the azaprismanes are similar in length to their counterparts in the azatetrahedranes. As before, there is a shortening of both the C–C and the C–N bonds as the number of nitrogens increases. Finally, the N–N distances are again unusually long, in the 1.58–1.60-Å range.

Among the azaprismanes being discussed are two sets of isomers, VII–IX and X, XI. At the 3-21G level, we find IX to be more stable than VII and VIII by 11.5 and 10.8 kcal/mol, respectively, while XI is more stable than X by 11.8 kcal/mol. In each set, the most stable isomer is the one having the fewest N–N bonds. (We found the same to be true for the isomeric tetraazaprismanes; only the results for the most stable one are being presented in this paper.)

We and others have found earlier that there is a considerable instability associated with the presence of two adjacent nitrogens in heterocyclic aromatic systems;³²⁻³⁶ we suggested that this may reflect, at least partially, a tendency to decompose through the evolution of N₂.^{35,36} While we are now again finding molecular instability to accompany N–N bonding, the same interpretation may not be applicable. The calculated N–N distances in the aromatic systems were in the 1.21–1.36-Å range, indicating intermediate to high degrees of double bond character. (The N=N bond lengths in H–N=N–H and F–N=N–F are about 1.25 Å.^{30,37}) In diazatetrahedrane and the polyazaprismanes, on the other hand, we find the N–N distances to be unusually long, roughly 1.59 Å (Table I). This suggests that the instability resulting from adjacent nitrogens in these strained molecules may be due to a tendency for the N–N bonds to rupture.

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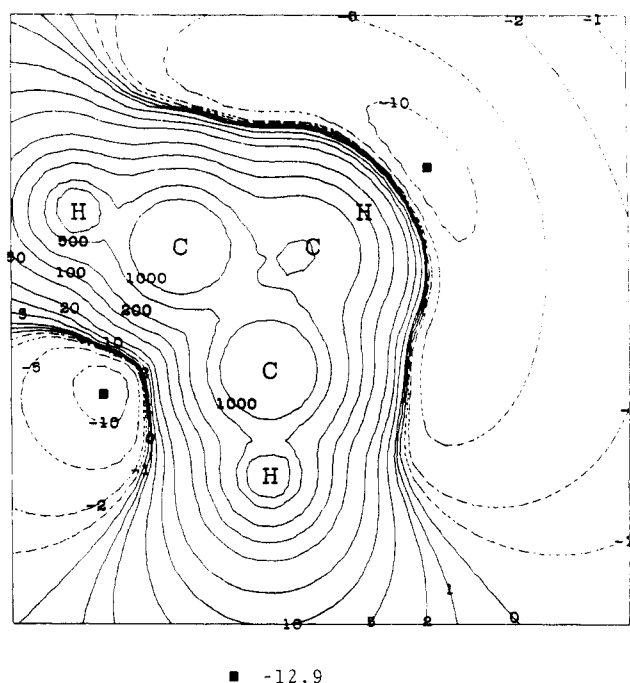
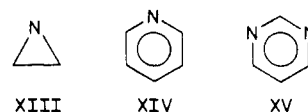


Figure 1. Electrostatic potential of tetrahedrane, I, in kcal/mol, in the mirror plane passing through one C–C bond and the midpoint of the opposite one. Dashed contours correspond to negative values. The actual or projected positions of the nuclei are indicated; the former can be identified by the presence of the +1000 contours. The locations of the most negative potentials are shown, and their magnitudes are given below the figure.

Bond Deviation Indexes. The bond deviation indexes of the C–C bonds in tetrahedrane (Table I) are the highest that we have yet encountered for any bond, which is consistent with the general perception of this as a very highly strained molecule. For comparison, the C–C indexes in cyclopropane and cubane (III) are 0.080 and 0.029, respectively,^{24,26} while in aziridine (XIII) they are 0.077 (C–C) and 0.069 (C–N). In the azatetrahedranes, the bond deviation indexes are still very high (Table I); thus these systems possess a great deal of strain. However, there is also a significant decrease in the λ values for each type of bond as the number of nitrogens increases, indicating that the strain is diminishing.



As has already been pointed out earlier,^{27,29} the bond deviation indexes for the two types of C–C bonds in prismane are very similar to those for cyclopropane and cubane (given above). From the standpoint of strain, therefore, prismane can be viewed as having cyclopropane-like bonds in the two three-sided faces and cubane-like links between these faces. Indeed the estimated strain energy of prismane (128 kcal/mol¹) can be reproduced quite closely by summing the strain energies of two cyclopropanes plus three of the faces of cubane:^{1,38}

$$2(28) + 3(157/6) = 134 \text{ kcal/mol}$$

Further indications of the special relationship of prismane to cyclopropane and cubane shall be found in their electrostatic potentials.

The C–N and N–N bonds in the azaprismanes have considerably lower bond deviation indexes than do either their counterparts in the azatetrahedranes or the C–C bonds in prismane; this is particularly striking for the N–N bonds and for the C–N in the three-sided faces containing two nitrogens (e.g., VIII). Moreover the effects of each new nitrogen are usually limited

(38) We thank Dr. Arthur Greenberg for bringing this to our attention.

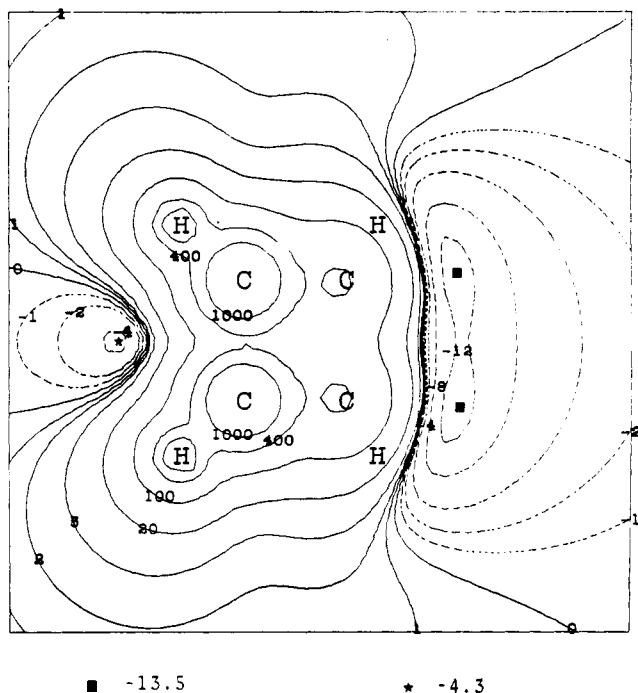


Figure 2. Electrostatic potential of prismane, II, in kcal/mol, in the mirror plane perpendicular to the three-sided faces, passing through one carbon in each of these faces and the midpoints of the opposite C-C bonds. Dashed contours correspond to negative values. The actual or projected positions of the nuclei are indicated; the former can be identified by the presence of the +1000 contours. The locations of the most negative potentials are shown, and their magnitudes are given below the figure.

primarily to the bonds in which it is directly involved. For example, the λ values for the cyclopropane-like face of VIII are very similar to those of prismane. Thus, while the bonds are less strained in the prismane systems than in the tetrahedranes, increasing the number of nitrogens does not necessarily diminish bond strain in the former.

Electrostatic Potentials. The calculated electrostatic potentials of tetrahedrane and prismane (Figures 1 and 2) show the interesting and significant feature of negative regions associated with the C-C bonds, the most negative points being near the midpoints of the bonds. While this is not at all typical of chemical bonds in general, we have found it to be characteristic of the C-C bonds in strained hydrocarbons.^{24,26-29,39} These bonds can accordingly serve as initial sites for electrophilic attack, as has indeed been observed in the laboratory. The olefin-like chemical properties of cyclopropane, which can undergo certain addition reactions, are one example;^{24,40,41} the cation-catalyzed rearrangements of cubane and homocubane are another.^{1,26,42,43}

It is noteworthy that the $V(\vec{r})$ minima for the two types of C-C bonds in prismane, -4.3 and -13.5 kcal/mol (Table I and Figure 2), are very similar to those found previously for cubane,²⁶ -4.6 kcal/mol, and cyclopropane,²⁴ -13.0 kcal/mol. This supports the earlier suggestion, based upon the calculated bond deviation indexes that these C-C bonds in prismane may be regarded as cubane-like and cyclopropane-like.

Due to the electron-withdrawing power of nitrogen, the negative C-C bond potentials are either greatly weakened or completely eliminated in monoazatetrahedrane, IV, and monoazaprismane, VI (Figures 3 and 4), and there are none at all in the di- and triaza systems. (This is so despite the fact that many of the bond

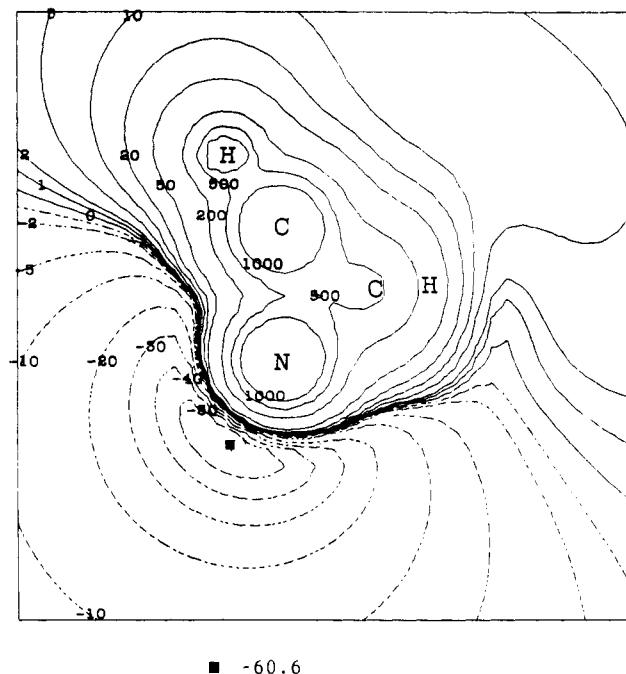


Figure 3. Electrostatic potential of azatetrahedrane, IV, in kcal/mol, in the plane passing through the C-N bond and the midpoint of the opposite C-C bond. Dashed contours correspond to negative values. The actual or projected positions of the nuclei are indicated; the former can be identified by the presence of the +1000 contours. The location of the most negative potential is shown, and its magnitude is given below the figure.

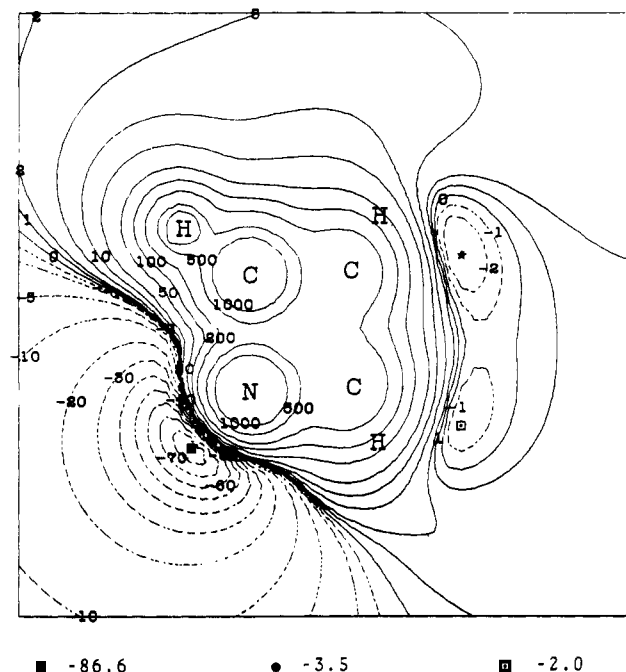


Figure 4. Electrostatic potential of azaprismane, VI, in kcal/mol, in the same plane as in Figure 2 but passing through a C-N bond. Dashed contours correspond to negative values. The actual or projected positions of the nuclei are indicated; the former can be identified by the presence of the +1000 contours. The locations of the most negative potentials are shown, and their magnitudes are given below the figure.

deviation indexes are quite high, which confirms again the absence of any direct relationship between the bond deviation index and negative bond potentials.^{24,29} Thus the reactivities of the C-C bonds toward electrophiles can be expected to greatly diminish as the number of nitrogens increases.

On the other hand, the azatetrahedranes and azaprismanes do show strong and extensive negative regions associated with the nitrogens, which can be attributed to their lone pairs (Figures 3-5).

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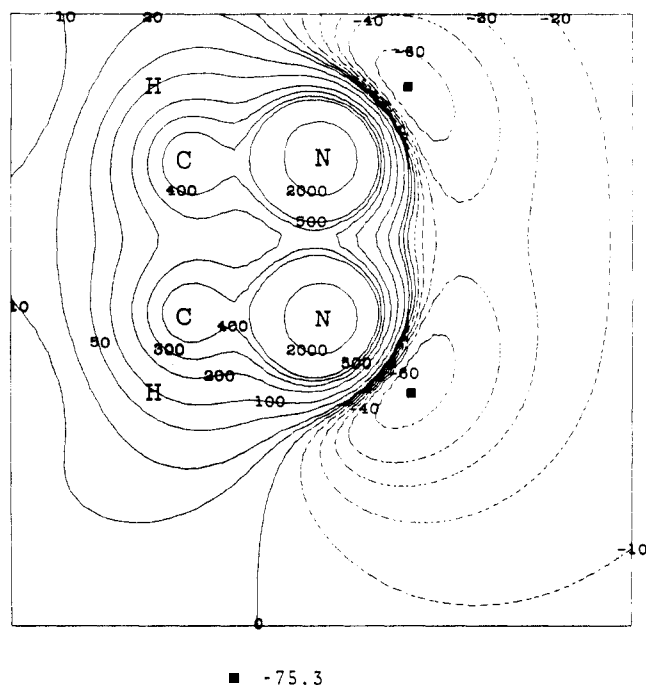


Figure 5. Electrostatic potential of diazaprismane, VII, in the plane passing through the N-N bond and perpendicular to the opposite four-sided face. Dashed contours correspond to negative values. The actual or projected positions of the nuclei are indicated; the former can be identified by the presence of the +1000 contours. The locations of the most negative potentials are shown, and their magnitudes are given below the figure.

These basic sites are expected to be important elements of the reactive behavior of the azasystems. Table I shows that these negative potentials become progressively weaker as the number of nitrogens in the molecule increases; as more of them compete for the available polarizable electronic charge, each receives a smaller share of it. The magnitudes of the minima decrease by roughly 10 kcal/mol for each additional nitrogen.

It may help put the chemical significance of these observations into better perspective to compare them to our recent results for some azabenzenes.³⁶ For pyridine, XIV, which has well-established basic properties and a measured pK_a of 5.2,⁴⁴ we found the nitrogen

electrostatic potential minimum to be -92.9 kcal/mol; for pyrimidine, XV, a weaker base ($pK_a = 1.1$), the minima are -84.1 kcal/mol.

It is interesting to note how much more negative the nitrogen potentials are in the azaprismanes than in the azatetrahedranes. For example, the three minima in the triazaprismanes are all more negative than the single minimum in monoazatetrahedrane. This may mean that the azaprismanes are more polarizable than the azatetrahedranes, but it may also reflect a similarity between the three-sided faces of the former and aziridine, XIII (which is suggested by their bond deviation indexes); the nitrogen potential in aziridine is -99.6 kcal/mol.

Summary

The major new points that have been brought out in this work are the following:

In tetrahedrane and its aza analogues, the C-C, C-N, and N-N bonds are quite highly strained; however, there is a distinct relaxation of bond strain as the number of nitrogens increases. In the prismanes, on the other hand, while the bonds are less strained, increasing the number of nitrogens does not necessarily diminish bond strain.

The negative electrostatic potentials associated with the C-C bonds in tetrahedrane and prismane are greatly weakened or eliminated as nitrogens are introduced, making these bonds less susceptible to electrophilic attack.

The nitrogens in the azaprismanes are more negative and accordingly more basic than those in the azatetrahedranes. In both types of systems, these basicities decrease as the number of nitrogens increases.

In each set of azaprismane isomers, the most stable is the one having the fewest N-N bonds. These bonds are exceptionally long, approximately 1.59 Å, perhaps reflecting a tendency toward rupture.

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