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Ab Initio SCF Study of the Disrotatory Closure of 1,4-Diaza-1,3-dienes to Diazacyclobutene

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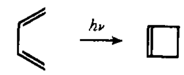
Abstract: An all-electron "ab initio" SCF–CI method is used to calculate the ground and lowest excited states potential energy surfaces for the "linear" reaction path of the disrotatory cyclization of α-diimine to diazacyclobutene. The analysis of these surfaces allows us to rationalize why this reaction, though very similar to the allowed and well-documented closure of butadiene into cyclobutene, is unlikely to occur.

Upon appropriate irradiation, 1,3-dienes may undergo two different electrocyclic reactions.[2] The first reaction, 4π-electron disrotatory closure (eq 1), leads to cyclobutene derivatives;[3] the second reaction, 6π-electron conrotatory opening (eq 2), leads to species characterized by a triene skeleton.[4] Both processes play a prominent role in the Woodward and Hoffmann qualitative analysis of allowed and forbidden electrocyclic reactions.[5] Moreover, the former has lately received quantitative attention.[6,7] 1,4-Diaza-1,3-dienes (α-diimines), though isoelectronic with butadiene, have a somewhat surprising photochemical behavior. These molecules are reluctant to form four-membered 1,2-diazacyclobutene rings by the 4π-electron photoclosure (eq 3).[8] On the other hand, the 6π-electron photovalence isomerization (eq 4) of 1,4-diaza-1,3-dienes into a triene-like structure occurs and has been convincingly documented.[9] This contrasting behavior between dienes and diazadienes could possibly be related to the one basic difference between their respective excited state manifolds: the presence in the latter of low-lying $n\pi^*$ excited states. These states result from the emergence in the diimine system of molecular orbitals of a pair of high-lying occupied n-type wave functions, that is, the familiar in-phase (n_+) and out-of-phase (n_-) combinations of the nitrogen lone pairs. In order to elucidate the rationale behind the "forbidden" character of (3) we have calculated the potential energy surfaces of several low-lying excited states of 1,4-diaza-1,3-dienes for the disrotatory distortion. We shall first briefly outline the profile of these calculations and then proceed to analyze the mechanistic implications of the resulting theoretical curves.



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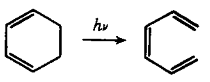

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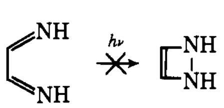

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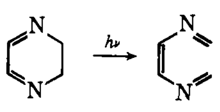

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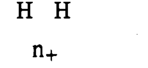

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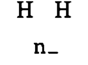


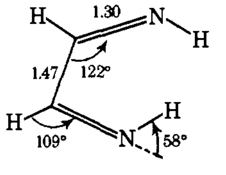
n_-

Method of Calculation. The disrotatory closure of α-diimine was investigated in a way which closely parallels our study of butadiene itself.[7a] The Gaussian 70 SCF program[10] was used to carry out the Hartree–Fock segment of the calculation. The basis set consists of two parts, that is, the familiar localized STO 3G valence atomic orbitals[11] were complemented by a set of semidiffuse Gaussian p orbitals with optimized exponents of 0.12 (carbon p orbitals) and 0.18 (nitrogen).[12] The three degenerate x, y, and z components were included on each carbon and nitrogen atom. This first SCF step must provide us with MO's which will serve to build the various Slater determinants forming the basis for the configuration interaction (CI) calculation. The best set of MO's must be obtained to ensure that the CI procedure, which for practical reasons, has to be limited, will nevertheless approach as closely as possible the results of a full treatment. In the vicinity of the reactant and product molecules, Roothaan's closed-shell SCF formalism[14] will undoubtedly give us adequate MO's. However, in the intermediate region of the reaction trajectory, where the rising highest occupied MO crosses the stabilized lowest vacant partner, more appropriate MO's are obtained by using Nesbet's brand of open-shell SCF calculation.[15] In fact, we have tried both methods at each point of the reaction path and accepted as final result that which, after completion of the CI, yields the lower energy for the ground state of te system. Finally the CI treatment was carried out in the following manner. The set of MO's whose occupancy is allowed to vary is the union of two smaller groups: (a) the n_+ and n_- pair and the eight π MO's of the diene plus those diene MO's which correlate with π MO's of the cycle and have not yet been counted, and (b) n_+ and n_- of the cycle, which correlate with their diene parents, respectively, the ten π MO's of the cycle plus those cycle orbitals which correlates with π MO's of the diene (prominent among them the σ and σ^* MO's of the newly formed N–N bond). All the one-electron configurations re-

Table I. Vertical Excitation Energies of the Low-Lying Excited States of 1,4-Diaza-1,3-diene and 1,2-Diazacyclobutene

	Ground-state absolute energies, au	
	1,4-Diaza-1,3-diene	Diazacyclobutene (cis)
SCF level	−184.6905	−184.6269
SCF–CI level	−184.7780 (reference)	−184.6682
	Ground and excited states relative energies, eV	
	1,4-Diaza-1,3-diene	Diazacyclobutene (cis)
$^{1}A_{1}$ (GS)	0	3.0
$^{1}B_{1}$ $(n_{+}\pi_{3})$	4.89	10.69
$^{1}A_{2}$ $(n_{-}\pi_{3})$	5.10	11.75
$^{1}B_{2}$ $(\pi_{2}\pi_{3})$	8.92	11.85
$^{1}A_{1}$ $(\pi_{2}\pi_{3})^{2}$	7.37	13.72
$^{3}B_{1}$ $(n_{+}\pi_{3})$	4.43	10.18
$^{3}A_{2}$ $(n_{-}\pi_{3})$	4.68	10.95
$^{3}B_{2}$ $(\pi_{2}\pi_{3})$	4.10	7.7

sulting from single or double excitations of the ground-state configuration were constructed and the corresponding CI matrix diagonalized.



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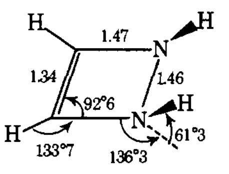

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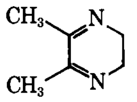
Both reactant **1** and product **2** geometries were optimized at the simple SCF (without CI) level using the Gaussian 70 SCF program with diazacyclobutene in the "cis" geometry which results from the disrotatory distortion of the diene.[16] Table I lists the ground-state energies and the excitation energies of the low-lying singlet and triplet excited states of both **1** and **2**. Several remarks seem appropriate. First, **1** is calculated to be 3 eV (69 kcal/mol) more stable than **2**. This difference, to our present knowledge, has not been experimentally evaluated, and we are forced to fall back on an approximate determination of this quantity using standard bond, delocalization, and strain energies.[17] A value of 78 kcal/mol is obtained, only 9 kcal/mol larger than our SCF-CI result. Let us also mention for comparison that a similar calculation for the butadiene–cyclobutene system leads to an energy difference of 12 kcal/mol in fair agreement with both the theoretical SCF-CI (17.4 kcal/mol) and experimental (8.9 kcal/mol) values.[7a] Let us now examine the position of the various $\pi\pi^*$ states.[19] The $^{3}B_{2}$ $(\pi_{2}\pi_{3})$ triplet lies 4.10 eV above the ground state. This energy gap matches closely the corresponding values in both butadiene, 3.93 eV (using an entirely similar theoretical framework[7a]), and glyoxal, 3.97 eV (single configuration SCF calculation with a double ζ basis set[20]). The parent $^{1}B_{2}$ singlet state is found at 8.92 eV. This value is undoubtedly overestimated since the completely diffuse AO's which would be necessary for an adequate description of this state to be achieved were not included in the starting basis set. Indeed the excitation energy of the parent state of butadiene is found to be 7 eV in a calculation which does include diffuse AO's.[7a] Still our value of 8.92 eV is in close agreement with a calculation of the $^{1}B_{2}$ state of *cis*-glyoxal (8.79 eV).[20] These results might possibly indicate an increase of the $^{1}B_{2}$ excitation energy along the butadiene, diimine, and glyoxal series. Let us also note the slow decrease exhibited by the vertical excitation energy of the doubly excited $(\pi_{2}\pi_{3})^{2}$ state (but see later our comments on the exact nature of this state) in the same series (7.4 eV in butadiene,[7a] 7.37 in diimine, and 7.24 in glyoxal[20]). Our final set of comments concerns the position of the pair of $n\pi_{3}$ excited singlet states. These are found 4.89 eV ($^{1}B_{1}$, $n_{+}\pi_{3}$) and 5.10 eV ($^{1}A_{2}$, $n_{-}\pi_{3}$) above the ground state. Some experimental informations on parent cyclic α-diimines are available.[9a,c] For example, in ethanol, 2,3-dimethyl-5,6-dihydropyrazine (**3**) presents an absorption spectrum with two bands respectively located at 337 mμ (ϵ 200, excitation energy 3.7 eV) and 230 mμ (ϵ 1740, excitation energy 5.39 eV). These values would seem to be in rather fair accord with their theoretical counterparts, and we would therefore be tempted to associate the 337 mμ band with a transition involving the $^{1}B_{1}$ $(n_{+}\pi_{3})$ state and its partner at 230 mμ with the $^{1}A_{2}$ $(n_{-}\pi_{3})$ state. Several facts, however, incite us to be cautious. We have performed an ab initio SCF-CI calculation on unsubstituted dihydropyrazine.[21] The $^{1}B_{1}$ $(n_{+}\pi_{3})$ level is found at exactly the same position as in the acyclic α-diimine **1** (4.90 eV) but the $^{1}A_{2}$ partner is pushed 1.15 eV higher in energy than its diazadiene analogue (this second state is found 6.25 eV above the 5,6-dihydropyrazine ground state). This displacement is undoubtedly due to a stabilizing two-electron through-bond interacton involving n_{-} and the in-phase combination of the antibonding σ^* MO's associated with the 23 and 56 C–C bonds. The discrepancy between the measured and calculated values is now in the 1 eV range, an error similar to that reported by Baird et al. in their study of 1,2-diaza species (0.87 eV).[22] It must also be noted that the excitation to the $^{1}B_{1}$ state is dipole allowed whereas that to $^{1}A_{2}$ is forbidden. In our tentative assignment the low-intensity band would then be associated with the allowed transition, the high-intensity one with the forbidden counterpart! Finally the 337 mμ band of **3** has been termed "anomalous" since it is only observed in six-membered rings and is absent or hidden in the parent five- or seven-membered cycles.[9a] Arnold has suggested this band to result from an excitation involving the ground state of **3** and an excited state of a second valence isomer, probably the enediimine **4**.



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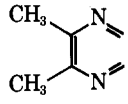

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Analysis of the Potential Energy Surfaces. Let us first emphasize that this analysis is not aimed at *proving* that reaction 3 cannot go. As pointed out by a referee, the prediction that a reaction cannot go because of no low-energy route would demand that many routes be explored. This would require an extensive investigation of the 19-dimensional hypersurface. This enormous job is, at the present time, impossible. Instead we wish to *compare* the potential energy surfaces of the excited states of α-diimine with those of its butadiene parent for similar reaction paths and thus gain some insight into the contrasting photochemical behaviors of these species.

As suggested by our previous experience with the butadiene-cyclobutene system,[7a] a "linear" reaction path has been investigated, that is, a path where all geometric variables are allowed to gradually change from their initial (diazadiene) to their final (diazacyclobutene) values by small increments proportional to the rotation θ of the NH groups ($\theta = 0°$ in the diene, 90° in the cycle). A unique symmetry element is conserved throughout the disrotatory distortion: the plane perpendicular to and bissecting the NCCN linkage. This plane will be referred to as the Cs plane. The various potential energy surfaces are represented in Figure 1, whereas Figure 2 sketches those obtained for the butadiene disrotatory closure.[7a] In the

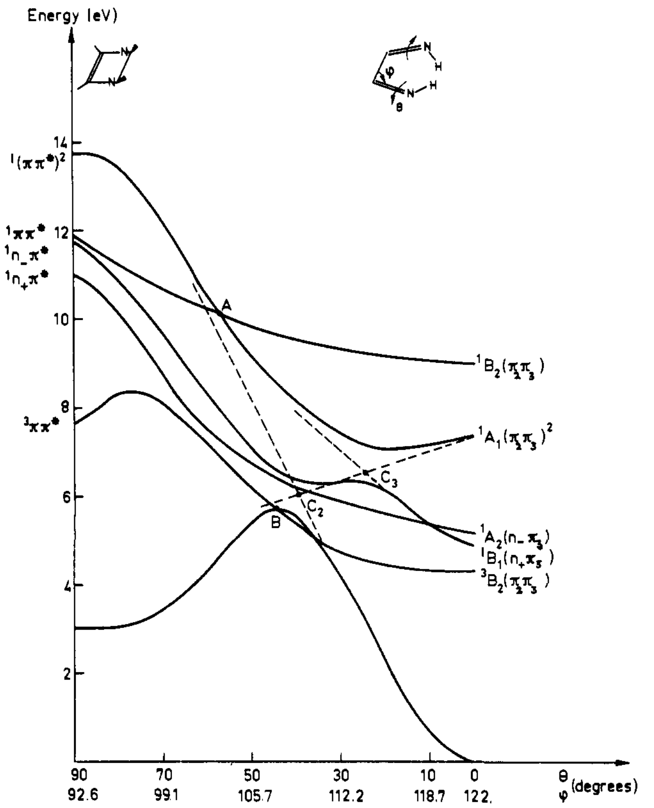

Figure 1. Potential energy curves for the low-lying states of the 1,4-diaza-1,3-diene–1,2-diazacyclobutene system in the linear path for the disrotatory closure reaction.

following discussion the potential energy surfaces will be described according to the diazadiene state which is their origin. For example, the $^1B_2$ surface designates the surface which starts at the $^1B_2$ $(\pi_2\pi_3)$ state of diimine.

Let us briefly recall the two prominent features of the butadiene system.[6,7] The first is an *avoided* crossing (at C_2) involving the two familiar ground state (diene or cycle)-doubly excited $(\pi\pi^*)^2$ state (cycle or diene) correlation curves (this is the avoided crossing which plays the central role in the Woodward and Hoffmann description of forbidden thermal reactions). The second is a *true* crossing which takes place at the very beginning of the reaction (C_1) and involves the singly excited $(\pi_2\pi_3)$ $^1B_2$ singlet and its doubly excited counterpart. These states are in a near-touching situation in butadiene itself, but $^1B_2$ raises in energy when the disrotatory distortion is turned on, whereas $^1A_1$ is stabilized, hence their crossing. These two crossings govern the intimate mechanism of the photochemical closure. The $^1B_2$ state is a "reservoir" of excited species. Those $^1B_2$ molecules endowed with 5 to 8 kcal/mol vibrational energy cross over the "valve" at C_1 to populate the neighboring well in the $^1A_1$ surface. This well, located 20 kcal/mol above the ground-state maximum, is a leakage channel (a "funnel"[23]) from the excited to the ground state.

The pattern of diazadiene excited state surfaces appears somewhat more confusing. The avoided crossing between the ground and doubly excited $(\pi\pi^*)^2$ states is still clearly apparent here. At the one-electron configuration level of description, the ground state of the diene (the cycle) correlates with the $(\pi\pi^*)^2$ state of the cycle (the $(\pi_2\pi_3)^2$ state of the diene). Both curves intersect at C_2. The associated wave functions are, however, symmetric with respect to the C_S plane and will be strongly mixed with each other in the vicinity of C_2 when the CI segment of the calculation is completed. As a result, a convenient leakage channel still exists which might bring excited species

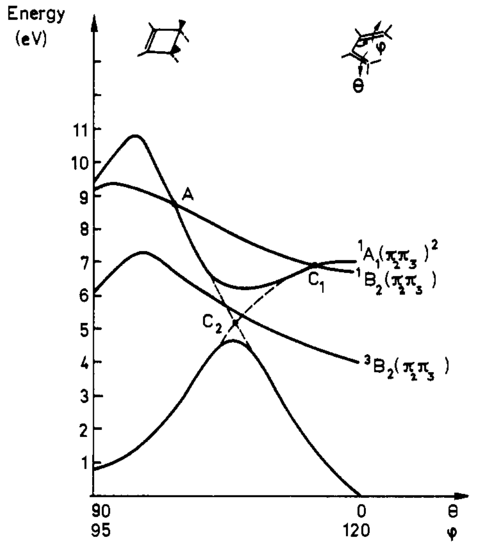

Figure 2. Potential energy curves for the lowest states of the butadiene–cyclobutene system in the linear path for the disrotatory closure of butadiene.

back to the ground-state curve. The analogy between butadiene and diazabutadiene ends at this point. The C_1 crossing is absent in the diazadiene system, and this diverging behavior may be traced to the complex nature of the $(\pi_2\pi_3)^2$ level. This denomination is only a convenient oversimplification. At the one-electron configuration stage, the doubly excited configuration $(\pi_2\pi_3)^2$ of a diene and the out-of-phase combination of the two singly excited functions $(\pi_1\pi_3)$ and $(\pi_2\pi_4)$, that is $1/\sqrt{2}\,\{(\pi_1\pi_3) - (\pi_2\pi_4)\}$, have similar overall symmetry (A_1) and comparable energies. The CI treatment mixes them very efficiently and, as a result, brings their out-of-phase combination (eq 5) down in energy.

$$(\pi_2\pi_3)^2 - 1/\sqrt{2}\,\{(\pi_1\pi_3) - (\pi_2\pi_4)\} \qquad (5)$$

In butadiene (5) is only 0.4 eV above the singly excited $(\pi_2\pi_3)$ singlet state. The situation is qualitatively analogous but quantitatively different in the diimine case. All one-electron configurations are now raised in energy as a whole as compared with their butadiene counterparts, but the matrix element which, in the CI process links the two parts of (5), is much larger (−5.30 eV) than in butadiene (−3.15 eV). As a consequence of this stronger interaction, the resulting out-of-phase combination (5), the so-called $^1A_1$ $(\pi_2\pi_3)^2$ state, is now shifted below the $^1B_2$ $(\pi_2\pi_3)$ state. When the disrotatory distortion is turned on, the former is stabilized, the latter raising in energy; their energy separation then increases. It is only after the C_2 avoided crossing ($\theta \sim 60°$) that the $^1A_1$ surface, now raising in energy but, in structure, more like the doubly excited $(\pi\pi^*)^2$ configuration of the cycle, intersects the $^1B_2$ surface (point A, also apparent in the butadiene case, Figure 2). Finally, the pattern of potential energy curves for the disrotatory closure of 1,4-diaza-1,3-diene is somewhat complicated by a second, and new, avoided crossing. We have already mentioned that the $(\pi_2\pi_3)^2$ configuration of α-diimine (which correlates with the cycle's ground state) participates in the C_2 avoided crossing. But even before reaching this leakage region, this configuration has been heavily contaminated by strongly mixing with the diimine $(n_+\pi_3)$ configuration which would tend to correlate with a high-lying doubly excited configuration $(n_+\pi_2 \rightarrow \pi_3{}^2)$ of diazacyclobutene. Both $(\pi_2\pi_3)^2$ and $(n_+\pi_3)$ functions have different symmetries at the starting C_{2v} diene geometry (A_1 and B_1, respectively). However, when the reaction proceeds, the collapse of C_{2v} into a C_S point group leaves these two states with similar transformation properties, that is, both become symmetric with respect to the C_S plane, and their mixing gradually develops with θ increasing from 0 to 25°. The C_3 avoided crossing region is also a convenient channel for $^1A_1$ $(\pi_2\pi_3)^2$ excited species to reach the $^1B_1$ surface. The C_2 channel in turn guides excited species from the latter onto the ground-state surface.

Let us now examine the reactive paths offered to the various excited states represented in Figure 1. The $^1B_2$ $(\pi_2\pi_3)$ state was the reactive state in the photochemical closure of butadiene. For a $^1B_2$ diimine to switch (point A) to the $^1A_1$ surface (and then via the pair of leakage channels reach the ground-state potential energy curve) would require an activation energy of 26 kcal/mol as compared with a mere 5 kcal/mol in the butadiene process. This value is much too large for A to be reached in a time compatible with the $^1B_2$ state's lifetime. The rather facile butadiene reaction trajectory thus becomes unrealistic in the diazadiene case, this being primarily due to the fact that $^1B_2$ is above $^1A_1$ $(\pi_2\pi_3)^2$ and the true C_1 crossing absent. Turning our attention to the parent $\pi_2\pi_3$ triplet state $^3B_2$, we observe that the $^3B_2$ surface crosses twice the ground-state surface in the vicinity of the latter's maximum. At these two intersections intersystem crossing might occur (though with a very feeble efficiency[24]) which would bring excited triplets back to the ground-state surface. As far as the closure process is concerned, only the second crossing (B) is relevant (the first would force the system back to the reactant). An activation energy of 32 kcal/mol is necessary for a $^3B_2$ excited species to attain point B and this path also appears to be doomed. We are then left with two candidates: the pair of $n\pi_3$ excited states. Starting from either of them, the most convenient path would be for an excited species to cross over the maximum in the $^1B_1$ surface in the vicinity of the C_3 avoided crossing, populate the adjoining shallow well, and then switch to the ground state via the C_2 funnel. Here again the activation energies which are needed are much too high for excited molecules to pass through the C_3 region in a photochemically reasonable period of time. Indeed $^1B_1$ $(n_+\pi_3)$ and $^1A_2$ $(n_-\pi_3)$ excited species must be endowed with, respectively, 33.6 and 27.6 kcal/mol vibrational energy. A second mechanism bringing an $n\pi_3$ excited molecule back to the ground-state potential energy curve might intervene.[25] Recall that the excitation energies of the $^1B_1$ and $^1A_2$ states are overestimated, roughly by 1 eV. Taking this error into account, crossings of the potential curves of these states with the ground-state one at points near B cannot be completely ruled out. However, these alternative reaction mechanisms would require activation energies of 33.6 kcal/mol ($^1B_1$ state, to reach the maximum at C_3) and ~24 kcal/mol ($^1A_2$ state, to reach B). Again these activation energies appear too large for the excited molecule to acquire them in a photochemically reasonable period of time.

None of the excited states we have discussed is therefore likely to initiate a closure of the diazadiene either because the very peculiar pattern of the $^1B_2$ $(\pi_2\pi_3)$ and $^1A_1$ $(\pi_2\pi_3)^2$ states of butadiene has disappeared in this parent case or because the additional $n\pi_3$ A_2 and B_1 singlet and triplet[26] states of α-diimine require prohibitive activation energies to reach the leakage well or the crossing point which would guide them back to the ground-state surface. It is true that these calculated activation energies are only higher bounds of the real quantities. They could undoubtedly be reduced by any improvement of our theoretical SCF-CI framework or, more likely, by a broader exploration of the full 19-dimensional potential energy hypersurfaces. More convicing than the calculation on the 1,4-diaza-1,3-diene system itself, however, is the comparison with the results we have found in our parallel study of the butadiene–cyclobutene reaction. It is our belief that the essential features that prevent the 4π-electron photoclosure of α-diimine to occur conform, at least semiquantitatively, to the results presented here.

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(12) These semi-diffuse AO's were added to further improve the description of the $\eta\pi$ excited singlet states. Indeed their exponents minimize the absolute energies of this duo of states. On the other hand the singlet $\pi\pi^*$ state will somewhat suffer from this procedure since its description would require totally diffuse AO's.[13] As far as this singlet is concerned, our mechanistic analysis should therefore be cautious.

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(16) The "trans" geometry which minimizes the repulsive four-electron term between the two nitrogen lone pairs is calculated to be 4.8 kcal/mol below its cis partner.

(17) We used the following standard bond energies (in kcal/mol): C=N, 147; C=C, 146; C–N, 73; C–C, 83; N–N, 39. In addition we admitted the delocalization energy of the diazadiene and the strain energy of the cycle to be similar to those of butadiene (6 kcal/mol) and cyclobutene (26 kcal/mol[18]), respectively.

(18) M. J. S. Dewar, "The MO theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, p 461.

(19) In the following discussion the excited states which result from the promotion of one or two electrons from MO a (filled in the ground state) to MO b (vacant in the ground state) are dubbed (ab) and $(ab)^2$, respectively.

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(21) The size of this system does not allow as much theoretical flexibility as the smaller diazadiene. The basis set used here consists only of the STO 3G valence AO's. To partially counterbalance this economically desirable restriction the CI was enlarged to include the singly and doubly excited configurations built on each excited state under scrutiny, that is, triple excitations of the ground-state one-electron configuration were added to the usual singly and doubly excited wave functions.

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(25) We are indebted to one of the referees for suggesting this possibility.

(26) We have not mentioned in the text the $^3B_1$ and $^3A_2$ triplet states of α-diimine. Their vertical excitation energies are 4.43 and 4.68 eV, respectively. Their potential energy curves are parallel to that of the $^1A_2$ singlet state. These two triplets appear to be unreactive for reasons similar to those exposed in the discussion of the $^3B_2$ state.