alternative procedures for peptide chains are underway in our laboratory.

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A Theoretical Study of the Disproportionation Reactions of N_2H_2 Species

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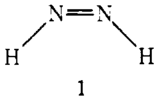
Abstract: Ab initio SCF calculations have been carried out on the disproportionation reactions of N_2H_2 (diimide) species to form dinitrogen and hydrazine. Concerted hydrogen transfer pathways for the reactions of *cis*- with *cis*- and *cis*- with *trans*-diimide possess lower energy barriers than does the reduction of ethene by *cis*-diimide, consistent with experimental observations. A two-step, hydrogen atom transfer process proceeding via N_2H and N_2H_3 radicals is also discussed and is considered to be an energetically feasible process for the disproportionation reaction. Calculations have also been carried out on the concerted transfer of hydrogen from 1,1-diimide (aminonitrene) to *cis*- and *trans*-diimide, these reactions having energy barriers substantially higher than for the transfer process involving *cis*-diimide.

Introduction

In a recent article we described the results of a theoretical study on the reactions of the various diimide species **1–3** with ethene.[1] The mechanistic implications derived from our study were in distinct contrast with those derived from earlier theoretical[2a] and gas-phase kinetic[3] studies in which the transfer of the hydrogens from **1** to ethene was indicated to be the rate-determining step instead of the isomerization of **2** to **1**. Our calculations indicated that the reaction of **1** with ethene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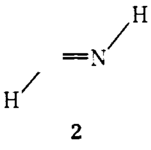
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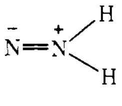
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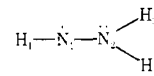
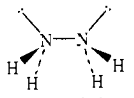
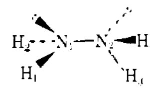
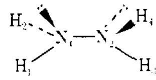
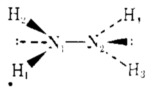
Table I. STO-3G and 4-31G Energies and Structures for Various N_2H, N_2H_2, N_2H_3, and N_2H_4 Species

	structural parameters	E, au (STO-3G)	E, au (4-31G)
N_2H	N=N, 1.233; N—H, 1.063; ∠NNH, 110.4°	−107.989 46	−109.231 21
1	N=N, 1.254; N—H, 1.060; ∠NNH, 111.5°	−108.545 06	−109.793 70
	(N=N, 1.229; N—H, 1.013; ∠NNH, 115.9°)[a]		−109.798 76[a]
2	N=N, 1.250; N—H, 1.059; ∠NNH, 103.4°	−108.555 73	−109.804 83
3	N=N, 1.289; N—H, 1.033; ∠NNH, 123.4°	−108.533 44	−109.795 01
	N—N, 1.431; H_1—N_1, 1.060; H_2—N_2, H_3—N_2, 1.029; ∠$H_1N_1N_2$, 102.3°; ∠$H_2N_2N_1$, ∠$H_3N_2N_1$, 110.7°; ∠$H_1N_1N_2H_2$, 44.0°; ∠$H_1N_1N_2H_3$, 162.8°	−109.156 00[b]	−110.393 89[c]
 (synperiplanar)	N—N, 1.483; H—N, 1.039; ∠HNN, 107.0°; ∠HNNH, 110.8°	−109.733 88	−110.974 54
 (synclinal)	N—N, 1.448; N_1—H_1, N_2—H_3, 1.041; N_1—H_2, N_2—H_4, 1.035; ∠$H_1N_1N_2$, $H_3N_2N_1$, 110.4°; ∠$H_2N_1N_2$, $H_4N_2N_1$, 107.2°; ∠$H_1N_1N_2H_4$, $H_3N_2N_1H_2$, 69.7°; ∠$H_1N_1N_2H_3$, 43.6°	−109.746 57	−110.993 45
 (anticlinal)	N—N, 1.455; H_1—N_1, H_3—N_2, 1.037; H_2—N_1, H_4—N_2, 1.033; ∠$H_1N_1N_2$, $H_3N_2N_1$, 109.8°; ∠$H_2N_1N_2$, $H_4N_2N_1$, 107.0°; ∠$H_1N_1N_2H_4$, $H_2N_1N_2H_3$, 112.1°	−109.747 07	−110.994 89
 (antiperiplanar)	N—N, 1.468; N—H, 1.038; ∠HNN, 104.1°; ∠$H_1N_1N_2H_3$, 71.0°	−109.750 12	−110.991 48
N_2	N≡N, 1.133	−107.500 65	−108.747 10

[a] Fully geometry optimized structural parameters and energy at the 4-31G level. [b] $\langle S \rangle^2 = 0.7574$. [c] $\langle S \rangle^2 = 0.7600$.

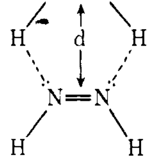
possessed the lower energy barrier. Later fully geometry optimized FORCE method calculations[2b] were in agreement with our results. The calculations also indicated that the transfer of hydrogens from **3** to ethene was a kinetically feasible process, and that **2** could undergo addition to ethene to produce ethylaminonitrene which in turn could be converted to ethane and nitrogen via a two-step, radical pair pathway.

A complicating feature of the diimide reduction of alkenes is that of disproportionation of "diimide" forming hydrazine and nitrogen. This in general requires the use of rather large excesses of the diimide source. As the diimide is formed in situ the steady-state concentration of diimide must remain very low, thus indicating that the disproportionation reaction(s) of the diimide species must possess energy barriers considerably below that for the reduction of C=C and C≡C. In the present article we describe the results of a theoretical study on the disproportionation reactions between the various diimide species.

Results and Discussion

Molecular orbital calculations using the GAUSSIAN 70 program[4] were carried out on structures along minimum energy pathways, transition states, and products at the STO-3G level using RHF for closed-shell and UHF for open-shell systems, with complete geometry optimization. Energies of reactants, complexes, transition states, and products have also been calculated at the 4-31G level on the STO-3G optimized structures (except as noted). The optimized structures and energies of the reactants[1] and products are summarized in Table I. It is interesting to note that the antiperiplanar conformation of hydrazine is the most stable at the STO-3G level, but that the anticlinal conformation is the most stable at the 4-31G level.

Cis Plus Cis. Although symmetry and orbital energy considerations would suggest that the transfer of the hydrogens of one molecule of **1** to another should involve transfer to the π system of **1** (i.e., involving FMO interactions between the b_2 HOMO and a_2 π^* LUMO of **1**), such is not the case.[1] Initial calculations indicated that the hydrogens are transferred to the predominantly nitrogen lone pair σ MO. Potential energy surface scan calculations as a function of the separation distance d in the two σ and π interaction configurations **4** and **5** gave energy minima at separation distances of 3.231 Å in **4** and 3.391 Å in **5**.[5] In both **4** and **5** the optimum structures have the axes of the N=N's parallel. Structure **5**, however, does not



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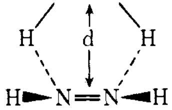

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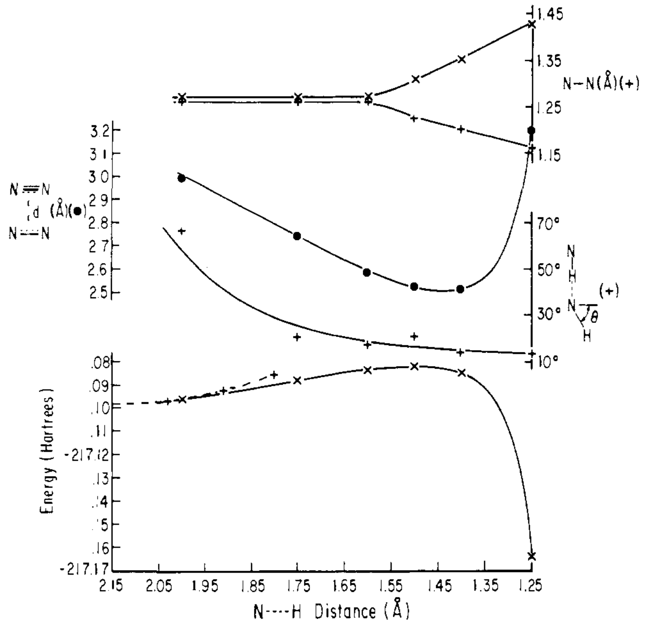


Figure 1. Profiles of total energy and selected geometrical parameters as a function of the N---H distance along the reaction coordinate for the disproportionation of *cis*-diimide.

represent an energy minimum structure similar to the type of π complex formed between **1** and ethene.[1] The preference for **4** over **5** arises from less nuclear repulsion present in **4**. Although the total electronic energy becomes *less* negative on conversion of **5** to **4** (−322.503 79 to −321.599 78 au at d = 3.231 Å), the nuclear repulsion decreases to a greater extent (105.412 91 to 104.501 00 au) thus making the total energy *more* negative (−217.090 87 to −217.098 78 au). **5** is converted to **4** without an intervening energy barrier. **4** lies 5.4 kcal/mol below the total energy of two **1**'s at an infinite separation distance. No energy barrier for the formation of **4** from separated **1**'s could be detected.

The character of the MOs of the individual **1**'s is predominantly retained in the hydrogen-bonded complex **4**. The interaction between the occupied MOs of the two **1**'s results in a substantial splitting of the energy levels (0.07–0.09 hartrees), the MOs of the lower **1** in **4** *all* being lowered. The Mulliken population analysis shows that the orbital interactions between the H's of the upper **1** and the N's of the lower **1** are bonding in nature and the interactions between the orbitals of the upper and lower N's are antibonding, with the former being greater than the latter.

The minimum energy pathway from **4** to the products N_2 and synperiplanar hydrazine was determined by carrying out full geometry optimization calculations (within C_s symmetry) at the STO-3G level at selected N---H distances (in **4**). The total energy was plotted vs. the N---H distance and the point of highest energy was taken as the transition state (see Figure 1). A final full geometry optimization calculation was carried out at that point, the results of which are illustrated in Figure 2. Figure 1 also shows how the various geometrical parameters change as a function of the N---H distance. The only parameter that changes markedly as the N---H distance decreases is the interplanar angle, or the rotation of the lower **1**. Rapid changes in the other parameters occur very shortly after passing through the transition state, in particular the exiting of the nitrogen molecule, similar to what was observed in the reaction of **1** with ethene.[1]

The energy barriers calculated for the disproportionation of **1** are 5.0 kcal/mol (10.4 kcal/mol from **4**) at the STO-3G level and 19.3 kcal/mol (27.3 kcal/mol from **4**) at the 4-31G level calculated on the STO-3G optimized structures. It was of some concern that the barrier calculated at the 4-31G level was significantly greater than that at the STO-3G level, and full geometry optimization calculations on **1** and partial geometry optimization calculations on the transition state were carried out at the 4-31G level (see Table I and Figure 2). The barrier thus calculated is 22.6 kcal/mol (from **1**), reasonably consistent with that calculated on the basis of the STO-3G optimized structures. The possibility that two energy levels of the transition state were close was also evaluated in view of the fact that there is a relatively low-lying virtual MO in the 4-31G calculation on the transition state. However, calculations initiated on an altered configuration indicated that the next closest energy level is considerably above that calculated for the transition state and that CI calculations would not greatly alter the magnitude of the barrier.

Cis Plus Trans. Potential energy surface scan calculations of **1** with **2** indicate the existence of a very weakly bound hydrogen bonded π complex at a separation distance of 3.30 Å which lies 0.50 (STO-3G) and 1.5 (4-31G) kcal/mol below the total energy of **1** plus **2** (see Figure 3). This hydrogen-bonded π complex is much less stable than the σ-type complex formed between two molecules of **1** and even that formed between **1** and ethene [1.4 (STO-3G) and 3.7 (4-31G) kcal/mol].[1]

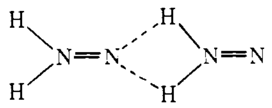
Calculations along the minimum energy pathway from the complex to the products nitrogen and anticlinal hydrazine were carried out as described above. The transition-state geometry and energies are given in Figure 3. The energy barriers for the disproportionation process, from **1** with **2**, are calculated to be 5.7 (STO-3G) and 23.8 (4-31G) kcal/mol. As before it is felt that the 4-31G value is more realistic.

1,1- Plus Cis. Potential energy surface scans on coplanar σ- and perpendicular π-type complexes revealed that only the coplanar σ complex represented an energy minimum structure, similar with that observed in the reaction of **1** with **1**. The complex lies 3.4 (STO-3G) and 6.0 (4-31G) kcal/mol below the combined energies of **1** and **3**. No energy barrier is observed in the formation of the complex.

In the conversion of the complex to products the rotation of the plane of **1** relative to that of **3** occurs much earlier along the reaction coordinate than in the case of **1** with **1**. The energy barriers for conversion of the complex to products are calculated to be 33.6 (STO-3G) and 47.1 (4-31G) kcal/mol. Figure 4 gives the structures of the complex and transition state and energies along the reaction coordinate.

1,1- Plus Trans. Potential energy surface scan calculations on a possible hydrogen-bonded complex indicate an extremely shallow energy minimum at a separation distance of 3.55 Å which lies 0.08 (STO-3G) and 0.9 (4-31G) kcal/mol below the reactants. Calculations along the minimum energy reaction pathway result in the transition state and energy shown in Figure 5. The energy barriers from the reactants are 29.8 (STO-3G) and 41.7 (4-31G) kcal/mol.

1,1- Plus 1,1-Diimide. Calculations on various reaction configurations (for example, **6** and **7**) gave increasingly higher



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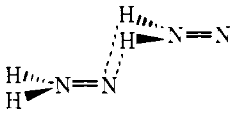

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energies (>100 kcal/mol above the reactants) as the N---H distances were decreased to ~1.4 Å either by horizontal displacement in **6** or vertical and/or horizontal displacements in **7**. As there were no indications in the results of the calculations that the total energies were reaching a maximum, further calculations were abandoned. Inspection of the Mulliken overlap populations showed that the N---H interactions became increasingly more antibonding as the N---H distances decreased.

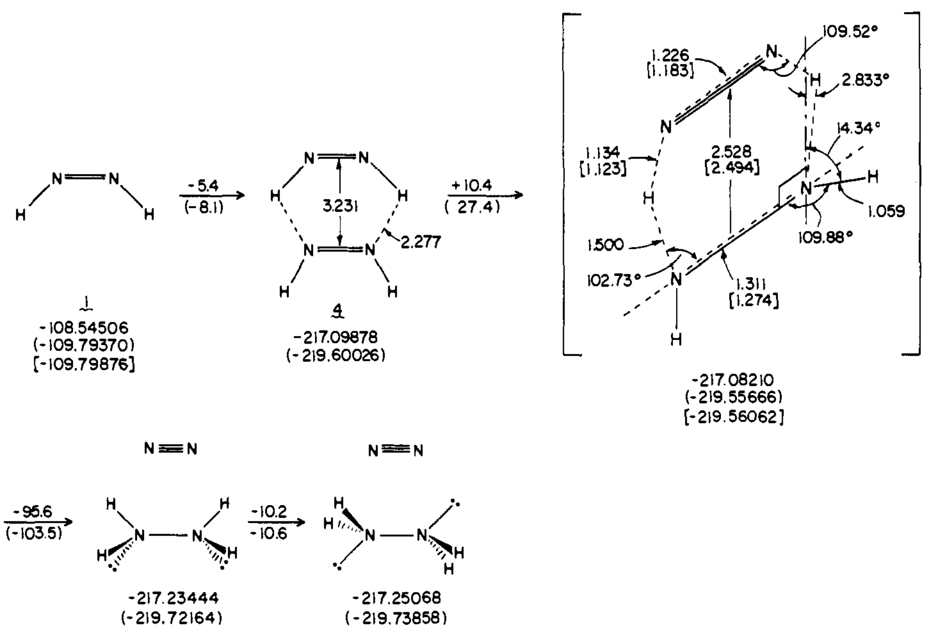


Figure 2. Structures and energies of the reactants, complex, transition state, and products in the disproportionation of *cis*-diimide. Energies not in parentheses are STO-3G values, while those in parentheses are 4-31G values. In the transition state the four nitrogen atoms lie in a plane.

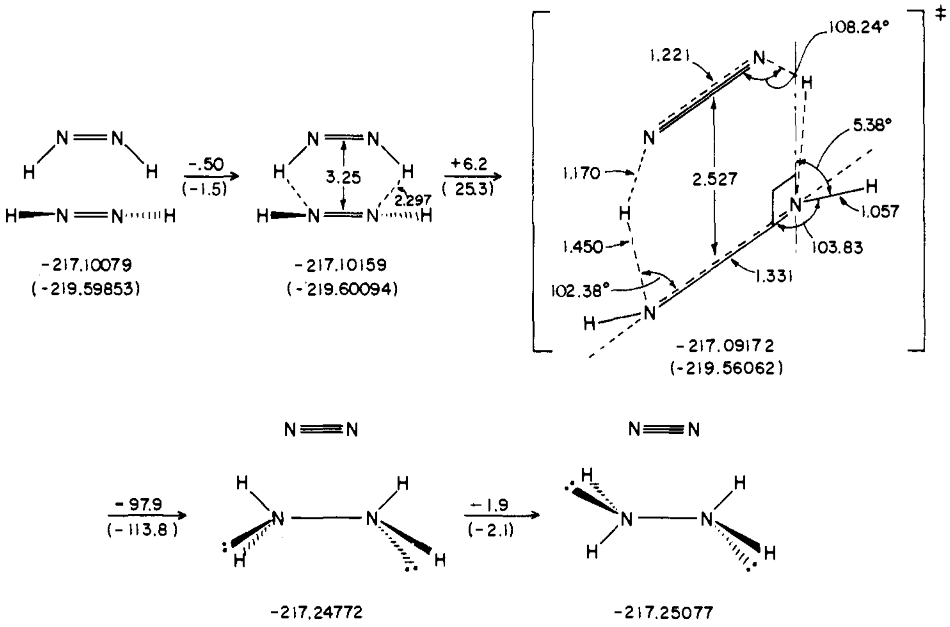
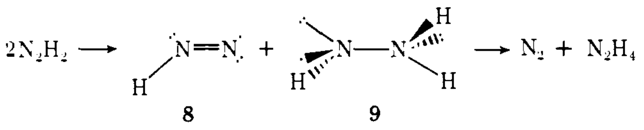


Figure 3. Structures and energies of the reactants, complex, transition state, and products in the reaction of *cis*- with *trans*-diimide. Energies not in parentheses are STO-3G values; those in parentheses are 4-31G values. The four nitrogen and two hydrogen (from *cis*-diimide) atoms lie in a common plane.

Disproportionation via Radical Pairs. The possibility that the disproportionation reactions of the N_2H_2 species could occur by a two-step, hydrogen atom transfer process via radicals **8** and **9** was also explored. The results of calculations on **8** were reported previously.[1,6] Fully geometry optimized STO-3G calculations have been carried out on the hydrazinyl



radical **9**. The structural parameters and energies of **8** and **9** are given in Table I, and the structure is illustrated in **9**.

Table II lists the energy differences between the various combinations of N_2H_2 species and **8** and **9**, and between **8** and **9** and the products nitrogen and antiperiplanar hydrazine. In all cases both of the hydrogen atom transfer steps are exothermic! Energy barriers for the hydrogen atom transfer steps have not been calculated because of the complexity of the calculations and the inability of RHF calculations to accurately describe such processes. It is not unreasonable that the energy barriers for these processes might be lower than those of the concerted processes described above.

Summary

Comparison of Energy Barriers for Disproportionation and Reduction of Ethene. Table III summarizes the overall energy barriers for disproportionation and reduction. Overall, the results are nicely consistent with experimental observations as outlined in the Introduction. The energy barriers for the

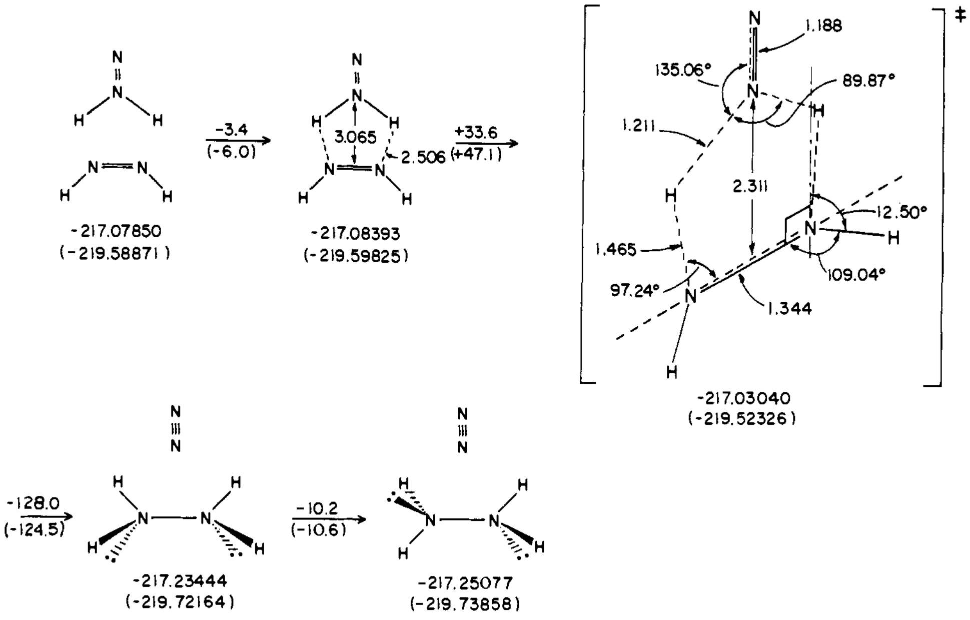


Figure 4. Structures and energies of the reactants, complex, transition state, and products in the reaction of 1,1-diimide with *cis*-diimide. Energies not in parentheses are STO-3G values; those in parentheses are 4-31G values. The four nitrogen and two hydrogen (of 1,1-diimide) atoms lie in a common plane.

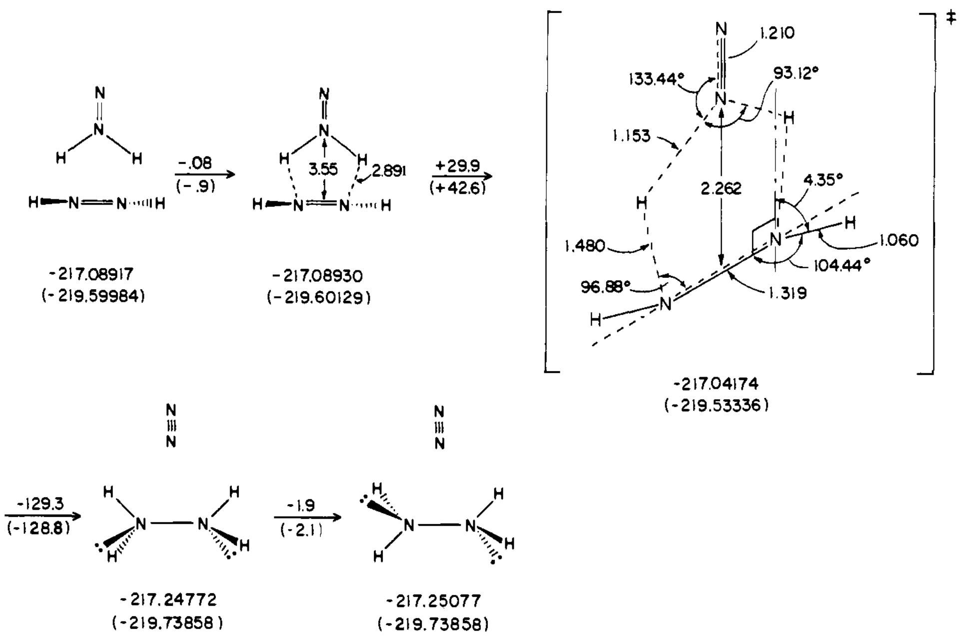


Figure 5. Structures and energies of the reactants, complex, transition state, and products in the reaction of 1,1-diimide with *trans*-diimide. Energies not in parentheses are STO-3G values; those in parentheses are 4-31G values. The four nitrogen and two hydrogen (of 1,1-diimide) atoms lie in a common plane.

Table II. Energy Differences between N_2H_2 Species and **8** Plus **9**, and between **8** and **9** and N_2 Plus N_2H_4

reactants	ΔE(STO-3G), kcal/mol	ΔE(4-31G), kcal/mol
	$2N_2H_2 \rightarrow \mathbf{8} + \mathbf{9}$	
1 + **1**	−34.7	−23.6
1 + **2**	−28.0	−16.7
1 + **3**	−42.0	−22.8
2 + **2**	−21.3	−9.7
2 + **3**	−35.3	−15.9
3 + **3**	−49.3	−22.0
	$\mathbf{8} + \mathbf{9} \rightarrow N_2 + N_2H_4$	
	−66.1	−71.2

Table III. Energy Barriers for Disproportionation and Reduction of Ethene at the 4-31G Level

reaction	*E*, kcal/mol
1 + **1**	19.3 (22.6)[a] (27.4)[b]
1 + **2**	23.8 (25.3)[b]
3 + **1**	41.1 (47.1)[b]
3 + **2**	41.7 (42.6)[b]
1 + $H_2C{=}CH_2$	26.7 (30.4)[b]
2 + $H_2C{=}CH_2$[c]	45.3 (45.8)[b]
3 + $H_2C{=}CH_2$	45.8 (47.7)[b]

[a] Result of fully geometry optimized 4-31G calculations on **1** and the transition state. [b] Energy barrier for conversion of complexes to products. [c] Energy barrier for formation of ethylaminonitrene.

disproportionation reactions of *cis*-diimide (**1**) with itself and with *trans*-diimide (**2**) are lower than that for reduction of ethene by **1**.

There essentially remains only one aspect of the diimide reduction reaction that still requires clarification. From a realistic point of view the reduction of a C═C or C≡C by N_2H_2 involves transfer of hydrogen only from *cis*-diimide (**1**). This demands that the less thermodynamically stable cis isomer be formed preferentially in order to attain the efficiencies in reductions that are observed. Only the thermal cycloreversion of the *cis*-diimide–anthracene adduct,[7] pyrolysis of *p*-toluenesulfonylhydrazine,[8] and the microwave discharge decomposition of hydrazine[9] are demanded to produce *cis*-diimide, and of these three processes only the second is adaptable to preparative-scale reactions. However, the most commonly used experimental procedures for the generation of diimide involve the oxidation of hydrazine[10] and the hydrolysis of azodicarboxylic acid[8,10,11] in which one would anticipate that the trans isomer should be preferentially formed. Thermal equilibration of the trans to the cis isomer is energetically precluded[1] under the normal experimental conditions. The only way in which to rationalize the efficiency of such reductions is to invoke a rapid, acid-catalyzed equilibration in aqueous or alcoholic solvents to continuously replenish the supply of the active reducing agent *cis*-diimide. Only experimental studies can resolve this aspect of the problem.

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On the Question of the Relationship of Nitrogen-15 Chemical Shifts to Barriers to C–N Internal Rotation. Dynamic Nuclear Magnetic Resonance of Urea and Aniline Derivatives

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Abstract: Dynamic ^{1}H and ^{13}C NMR effects resulting from restricted internal rotation about C–N bonds are observed in tetramethylurea (**1**), tetramethylthiourea (**2**), *N*-methylaniline (**3**), and *p*-nitro-*N*-methylaniline (**4**) in the temperature range 0 to −150 °C. The free-energy barriers for C(═X)–N internal rotation in **1** and **2** are both 6.3 kcal/mol and do not agree with barriers recently predicted for these compounds from ^{15}N chemical shift data. The barrier found for **1** by means of line-shape measurements agrees with a previously determined value obtained by a $T_{1\rho}$ technique. A reason for the failure of the predictions based on chemical shifts is presented. The barrier to C–N internal rotation in **3** is 6.1 kcal/mol, and is in reasonable agreement with barriers predicted from ^{15}N chemical shifts and from a Hammett relationship. The barrier to internal rotation in **4** is distinctly solvent dependent, being larger in acetone-d_6 (11 kcal/mol) than in CD_2Cl_2 (10.2 kcal/mol). The barriers predicted for **4** on the bases of ^{15}N chemical shifts and of the Hammett relationship are in fair agreement with the experimental value.

The chemical shift of ^{15}N is known to be dominated by the paramagnetic term in the usual expression for the chemical shift of a nucleus in a molecule.[1] The paramagnetic term is strongly dependent on the amount of π bonding at the nitrogen atom.[1] Since barriers to internal rotation about C–N bonds in many compounds are also strongly dependent on π bonding, it is understable that there should be a correlation between free-energy barriers for C–N internal rotation and ^{15}N chemical shifts.[2] Clearly, molecules where the origin of the barrier is steric have to be excluded. Even then, different classes of compounds, e.g., amides, thioamides, and anilines, give separate correlation lines. It has been suggested[2] that ^{15}N chemical shifts provide a way of evaluating C–N bond rotational barriers in molecules where conventional dynamic NMR techniques may not be applicable. That such predictions may not be entirely reliable is indicated by the recent report[3] that the barrier to rotation in tetramethylurea (**1**), as obtained from $T_{1\rho}$ measurements at −115 to −120 °C, is only 6.1 kcal/mol, compared to a predicted value of 11.6 kcal/mol.[2a] In view of the somewhat indirect nature of $T_{1\rho}$ measurements, we have made direct dynamic NMR measurements on **1**, and also on tetramethylthiourea (**2**), *N*-methylaniline (**3**), and *p*-nitro-*N*-methylaniline (**4**), compounds whose barriers have not previously been measured directly, although the barriers have