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The Ground-State Potential Energy Surface of Diazene

Hans Jørgen Aa. Jensen,[†] **Poul Jørgensen,**[†] **and Trygve Helgaker***

Contribution from the Departments of Chemistry, Aarhus University, DK-8000 Århus C, Denmark, and University of Oslo, Blindern, Oslo 3, Norway. *Received September 10, 1986*

Abstract: Using a multiconfigurational self-consistent-field wave function we have carried out a uniform study of the ground-state potential energy surface of diazene. We have determined the equilibrium structures and the reaction paths leading to six transition-state structures. We contest the reaction paths previously calculated by Pople et al., Casewit and Goddard, and Dykstra for the unimolecular shift of hydrogen in the *cis*-diazene ↔ *trans*-diazene and isodiazene ↔ *trans*-diazene isomerization reactions. The harmonic force fields of the equilibrium structures have been calculated and are compared with the available experimental data. Assignments to the infrared spectrum of *cis*-diazene by Rosengren and Pimentel and Wiberg et al. have previously been contested based on analogies with substituted diazenes; our calculations show that the assignments may be correct.

I. Introduction

Diazene (N_2H_2) is an important chemical compound which is used synthetically in the selective reduction of nonpolar bonds[1] and as ligands in transition metal complexes.[2] It is also the parent molecule for a large number of azo compounds. Diazene has therefore been the subject of numerous investigations, both experimental[3-6] and theoretical.[7-19]

It is now firmly established that diazene has a singlet ground state of C_{2h} symmetry (*trans*-diazene). Evidence for this comes from vibrational spectroscopy (see Craig and Levin[4] who critically review previous work), high-resolution infrared spectroscopy,[5] and theoretical studies.[7] The experimental evidence for *cis*-diazene is more sparse, with only a few fundamentals tentatively assigned.[3] However, theoretical investigations indicate that this isomer of C_{2v} symmetry is 24–32 kJ/mol higher in energy than its trans counterpart.[7-9] Finally, very little is known about the third isomer of diazene, in which both hydrogens are attached to the same nitrogen (isodiazene). Previous theoretical studies conclude that this isomer has C_{2v} symmetry and lies 100–120 kJ/mol above the trans isomer.[7,8] Recently Sylwester and Dervan[6] have observed the NN stretching of isodiazene in a matrix isolation experiment.

Much of the theoretical work on diazene has been concerned with the mechanisms for interconversion between its three isomers, in particular the hydrogen shifts which occur during the trans–cis and trans–iso rearrangements. The discussions have been based on estimates of the activation energy, i.e., the difference between the total energies calculated at the equilibrium and transition-state geometries. Such procedures are reliable only if the total energy is described to the same accuracy at all geometries. However, in many cases the equilibrium and transition-state geometries have been calculated using wave functions of different quality. In particular, owing to difficulties in optimizing transition-state structures, these geometries have often been calculated using a wave function of lower accuracy (for example, Hartree–Fock) than that used at the stable geometries. In some cases corrections have been introduced by recalculating the energy at the transition state using a more accurate wave function. However, this hardly improves the situation since the location of the transition state may be very different for the two wave functions. This is especially critical in cases where the transition state is sharp, since in such cases apparently insignificant changes in geometry may produce large changes in the energy.

Because of recent progress in evaluating molecular Hessians (second derivatives of the energy with respect to geometrical displacements) analytically,[20] it has become more straightforward to determine transition states using accurate wave functions. In a recent article, we have demonstrated how transition states may be determined in a modest number of iterations (wave-function calculations) for multiconfigurational self-consistent-field (MCSCF) wave functions[21] using a restricted-step (trust region) optimization technique.[22]

In the present article we report a detailed study of the diazene singlet ground-state potential energy surface. Uniform accuracy at all geometries is achieved by using a complete active space (CAS) MCSCF wave function generated by distributing eight electrons among eight orbitals. The geometries of the three stable isomers and six transition states have been optimized. Each transition state was determined in a completely automatic manner by carrying out a walk that starts out along a given normal coordinate at one of the equilibrium geometries and follows a streambed until a transition state is reached. This gives us a reaction path as a byproduct of the optimization.

The calculated equilibrium structures of *trans*- and *cis*-diazene compare well with previous calculations and experimental data. However, somewhat surprisingly the structure of isodiazene is found to be slightly distorted from C_{2v} symmetry. Calculations at a higher level of accuracy did not change this result, but we still feel that more elaborate calculations must be carried out to settle this question. [See Note Added in Proof.]

[†] Aarhus University.

[*] University of Oslo. Present address: Institute for Mathematics and Its Applications, University of Minnesota, Minneapolis, MN 55455.

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The quadratic force fields of *trans*-, *cis*-, and isodiazene were calculated by diagonalizing the mass-weighted Hessian at the optimized geometries. The force field of *trans*-diazene compares well with the empirical force fields of Craig and Levin.[4] The force field calculated for *cis*-diazene differs from the force field predicted by these authors[4] but is in agreement with the early assignments of Rosengren and Pimentel.[3]

Previously the transition state connecting *trans*- and *cis*-diazene has been assumed to correspond to inversion at one nitrogen atom rather than internal rotation around the N=N bond.[8,10,16,19] This conclusion was based on a rather crude optimization of the rotation barrier using a two-configuration SCF wave function.[19] Our calculations strongly indicate that the rotation and inversion energies are very similar and slightly above the activation energy for the N_2H + H dissociation pathway. The transition state corresponding to internal rotation is extremely narrow, indicating high probability of tunneling in this case.

For the trans–iso rearrangement we find that the out-of-plane transition state, which has been determined in previous Hartree–Fock calculations,[11,16] becomes planar when an MCSCF wave function is used. The activation energy of the in-plane transition state is found to be substantially higher than for the N_2H + H dissociation pathway. We also find that the diazenyl radical N_2H is unstable since the calculated minimum is too shallow to accommodate a vibrating molecule.

With respect to the Woodward–Hoffmann symmetry rules, we find that these cannot be applied to the formation of diazene.

II. Computational Details

In all calculations reported we have used Tatewaki's (421/21) split-valence basis on nitrogen[23] augmented with a set of d polarization functions (exponent 0.864).[23] On hydrogen Dunning's 2s contraction of Huzinaga's 4s basis[24] was used with a set of p polarization functions added (exponent 1.000). We note that Tatewaki's basis set[23] is specifically designed to give a flexible representation of the valence shell at the expense of the 1s core orbital, and that this may lead to somewhat high total molecular energies. A complete active space (CAS) was constructed from the 2p orbitals on nitrogen and the 1s orbitals on hydrogen. The wave function was calculated using the SIRIUS MCSCF program.[25]

Equilibrium and transition-state geometries were determined using the restricted-step (trust region) algorithm described elsewhere.[21] This algorithm makes efficient use of the first and second derivatives of the potential energy (the molecular gradient and Hessian) to locate and characterize stationary points. In particular, transition states are determined by walking away from an equilibrium geometry following a given Hessian eigenvector along a streambed (reaction path) until a saddle point with one and only one negative Hessian eigenvalue is encountered. This procedure does not depend on any previous guess or knowledge of the location of the transition state.

In our implementation of the restricted-step algorithm the molecular gradient and Hessian are calculated analytically in each iteration using the ABACUS program.[20] At the stationary points diagonalization of the mass-weighted Hessian yields the harmonic frequencies. Combining this with analytically calculated dipole derivatives,[26] we also obtain the double harmonic infrared intensities.

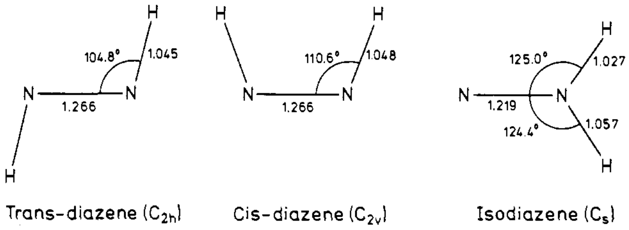

Figure 1. The equilibrium structure calculated for *trans*-diazene, *cis*-diazene, and isodiazene. [See Note Added in Proof.]

Table I. Energies for Equilibrium and Transition-State Structures[a]

species	E_{pot}	E^0_{vib}	ΔH_0
trans	−109.946 656	73.4	303.1
cis	−109.935 549	72.2	331.1
iso	−109.890 805	71.5	447.8
TS1	−109.839 936	56.5	566.4
TS2	−109.842 048	63.8	568.2
TS3	−109.843 900	25.5	525.0
TS4	−109.809 130	54.4	645.4
TS5	−109.812 361	50.4	632.7
N_2H	−109.346 077	29.9[b]	
N_2	−108.899 566	14.1	
H_2	−1.149 694	25.6	
H	−0.497 637	0	
N_2H + H (TS6)	−109.843 714	29.9[b]	529.9[b]
N_2 + 2H	−109.894 840	14.1	107.8
$N_2 + H_2$	−110.049 260	39.7	0.0

[a] Electronic and nuclear potential energy (E_{pot}) in atomic units, zero-point vibrational energy (E^0_{vib}) in kJ/mol, and enthalpy at 0 K relative to $N_2 + H_2$ (ΔH_0) in kJ/mol. [b] N_2H is unstable when zero-point vibrational energy is added.

The diazene potential energy surface was investigated in the following manner. First the three equilibrium structures (*trans*-, *cis*-, and isodiazene) were determined and analyzed. In particular, the harmonic force constants, harmonic frequencies, and double harmonic infrared intensities were calculated. Transition states connecting these equilibrium geometries or leading to fragmentation of the molecule were then determined by following selected normal coordinates at each geometry. Finally, the harmonic frequencies (including the imaginary frequency associated with the reaction coordinate) were calculated at the saddle points. All stationary points were converged to an accuracy of 10^{-4} in the molecular gradient. Each transition-state walk required typically 10 iterations.

At each equilibrium geometry the Hessian eigenvalues separate into two distinct classes: one containing three low-lying modes and another containing three higher modes. Transition-state walks were carried out along all lower modes in both directions from all three geometries. Also, most of the higher modes were investigated. However, when the higher modes were followed, bifurcations were encountered resulting in a Hessian structure that cannot be treated using the present algorithm. Such walks were abandoned. In most of these cases the total energy was so high that the reaction path has little or no chemical interest.

III. Equilibrium Structures

(a) Geometries and Energies. The optimized equilibrium structures of *trans*-, *cis*-, and isodiazene are reported in Figure 1. The experimental geometry is only known for *trans*-diazene (r_{NN} = 1.252 Å, r_{NH} = 1.028 Å, and θ_{NNH} = 106.8°).[5] Our calculation is in reasonable agreement with this geometry, the deviations in bond lengths and bond angles being 0.02 Å and 2°, respectively.

The *trans*-, *cis*-, and isodiazene equilibrium geometries have been calculated previously by several authors.[7-9] Our trans and cis geometries compare well with calculations which use an orbital basis and a wave-function approximation of the same quality as ours. However, the optimized structure of isodiazene displays an unexpected distortion from C_{2v} symmetry which has not been observed in previous calculations. To investigate this further we calculated the wave function of isodiazene at an averaged C_{2v} geometry. This resulted in a symmetry-broken wave function except when symmetry was explicitly enforced during the MCSCF optimization. Also an extended calculation with two additional orbitals in the active space displayed the same behavior. We feel that larger and more elaborate calculations must be carried out before it finally can be decided whether or not isodiazene is

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Table II. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for *trans*-Diazene[a]

	HNNH					DNND					HNND			
	calcd freq	exptl freq	calcd intens	mode		calcd freq	exptl freq	calcd intens	mode		calcd freq	exptl freq	calcd intens	mode
A_g	3154	3128	0	NH str	A_g	2308	2320[d]	0	ND str	A′	3176	3124	38	NH str
	1663	1583	0	NH bd		1523	1539	0	NN str		2322	2310	18	ND str
	1526	1529	0	NN str		1272	1215	0	ND bd		1562	1481	22	NH bd
A_u	1351	1289[b,c]	76	torsion	A_u	987	946	41	torsion		1524	1536	0.3	NN str
B_u	3197	3120[c]	73	NH str	B_u	2336	2315[c]	39	ND str		1096	1058	41	ND bd
	1374	1316[b,c]	81	NH bd		1004	972	43	ND bd	A″	1183	1131	59	torsion

[a] Experimental frequencies from Craig and Levin, ref 4. [b] Reference 28. [c] From gas-phase spectra. All others from nitrogen matrices. [d] Estimate based on the product rule.

Table III. Valence Force Constants for *trans*-Diazene[a]

		experimental[b]		SQM	
	ab initio	eight-parameter function	seven-parameter function	scaled to HNNH	scaled to DNND
f_R	10.30	10.56 (19)	10.59 (14)	10.36 (17)	10.52 (20)
f_r	5.605	5.388 (47)	5.418 (21)	5.424 (65)	5.585 (78)
f_α	1.292	1.175 (34)	1.144 (10)	1.177 (14)	1.193 (16)
f_γ	0.5162	0.446 (6)	0.446 (6)	0.4699 (76)	0.4740 (83)
f_{Rr}	0.335	0.0	0.0	0.330	0.338
$f_{R\alpha}$	0.686	0.667 (55)	0.675 (39)	0.657	0.666
$f_{rr'}$	−0.056	0.0	−0.027 (26)	−0.054	−0.056
$f_{r\alpha}$	0.100	0.25 (11)	0.0	0.094	0.096
$f_{r\alpha'}$	0.101	−0.25 (16)	0.0	0.095	0.097
$f_{\alpha\alpha}$	0.149	0.091 (25)	0.115 (11)	0.136	0.138

[a] Units are mdyn/Å for stretching, mdyn Å for bending, and mdyn for stretch–bend interactions. [b] From Craig and Levin, ref 4.

distorted from C_{2v} symmetry.[21] [See Note Added in Proof.]

In Table I we report the total electronic potential energies E_{pot} and the zero-point vibrational corrections E^0_{vib} for the three stable diazene isomers. The zero-point vibrational energies are determined from the harmonic fundamentals obtained by diagonalizing the mass-weighted molecular Hessian (see Tables II, V and VII). Also listed are the enthalpies at 0 K relative to $N_2 + H_2$. The enthalpies of *cis*- and *trans*-diazene are about 20 kJ/mol higher than those calculated by Brandemark and Siegbahn[9] using a similar wave function at the triple-ζ level. Only by carrying out extensive configuration interaction (CI) calculations including the Davidson correction were Brandemark and Siegbahn able to obtain an enthalpy close to the experimental value of 219.2 ± 8 kJ/mol.[27]

The calculated enthalpy differences between *cis*- and *trans*-diazene is 28.0 kJ/mol which is close to the MCSCF value of 26.8 kJ/mol reported by Brandemark and Siegbahn.[9] Brandemark and Siegbahn show that extensive CI significantly lowers this value. Enthalpies close to ours were obtained by Parsons and Dykstra[8] using a self-consistent electron pair (SCEP) wave function. Parsons and Dykstra have also reviewed previously calculated enthalpies for the *cis*- → *trans*-diazene isomerization and for the iso- → *trans*-diazene isomerization. We calculated the latter enthalpy to 144.7 kJ/mol which is significantly higher than the best SCEP value of 102.5 kJ/mol reported by Parsons and Dykstra[8] and previously reported values.[8]

(b) Vibrational Analysis. The fundamental frequencies and infrared intensities of *trans*-diazene are reported in Table II. The overall agreement between experimental[4] and calculated frequencies is reasonable (average deviation being 3%) considering: (i) neglect of anharmonic contributions to calculated frequencies, (ii) uncertainties in the experimental values due to matrix effects which affect most of the observed data, and (iii) differences in molecular geometries (calculated and experimental values). The conclusions that may be drawn from these comparisons are that our wave function gives an adequate description of the potential energy surface around the *trans*-diazene equilibrium geometry, and that the assignments of Craig and Levin[4] are correct. In particular, the close proximity of the two infrared-active nonstretching modes is supported. The difference between antisymmetric deformation and torsion is 23 cm^{-1} (experimental value 27 cm^{-1}) in HNNH and 17 cm^{-1} (experimental value 26 cm^{-1}) in DNND. Similarly the difference between NND bending and torsion in HNND is calculated to be 87 cm^{-1} (experimental value 73 cm^{-1}). We also note that for HNNH and DNND all infrared-active modes are predicted to be equally intense.

It is interesting to note that the discrepancies between the theoretical and experimental frequencies decrease from 3.0% in HNNH through 2.8% in HNND down to 2.4% in DNND. This is apparently related to the fact that vibrations affecting deuterium are less anharmonic than vibrations involving proton, since the mean-square displacements of deuterium are smaller than those of proton. This tendency is especially pronounced for the NH and ND stretching modes, where the discrepancies are 1.7% in HNNH and 0.7% in DNND.

In Table III various internal valence force fields for *trans*-diazene are listed. In particular, the ab initio harmonic force field obtained from our wave function is compared with the two empirical force fields of Craig and Levin,[4] both based on the frequency assignments in Table II. [Craig and Levin used slightly different values for torsion (1286 cm^{-1}) and antisymmetric deformation (1322 cm^{-1}) in HNNH. We have preferred to report the more recent gas-phase values by Hallin et al.[28] for these vibrations.] The most conspicuous difference between the ab initio and empirical force fields is the significantly higher values for the bending constants f_α (in-plane deformation) and f_γ (out-of-plane torsion) of the theoretical force field. Comparisons with the coupling constants are less conclusive because the empirical force fields are incomplete because of insufficient experimental data. However, the agreement between calculated and experimental values for $f_{R\alpha}$ and $f_{\alpha\alpha}$ is reasonable. A rather unusual feature of the theoretical force field is the positive values of both the $f_{r\alpha}$ and $f_{r\alpha'}$ coupling constants, in disagreement with the eight-parameter force field of Craig and Levin and also with a general trend in many molecules.

Empirical force fields for *trans*-diazene have also been determined by Nibler and Bondybey.[29] Although these force fields are more complete than those of Craig and Levin, the dispersions in many of the coupling constants are several times larger than

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Table IV. Valence Force Constants for *cis*-Diazene[a]

	ab initio	empirical[b]		ab initio	empirical[b]
f_R	10.42	10.75	$f_{R\alpha}$	0.712	0.669
f_r	5.366	4.89	$f_{rr'}$	0.115	−0.027
f_α	1.296	1.10	$f_{r\alpha}$	0.023	0.0
f_γ	0.389	0.394	$f_{r\alpha'}$	−0.117	0.0
f_{Rr}	0.222	0.0	$f_{\alpha\alpha'}$	0.026	0.115

[a] Units are mdyn/Å for stretching, mdyn Å for bending, and mdyn for stretch–bend interactions. [b] From Craig and Levin, ref 4.

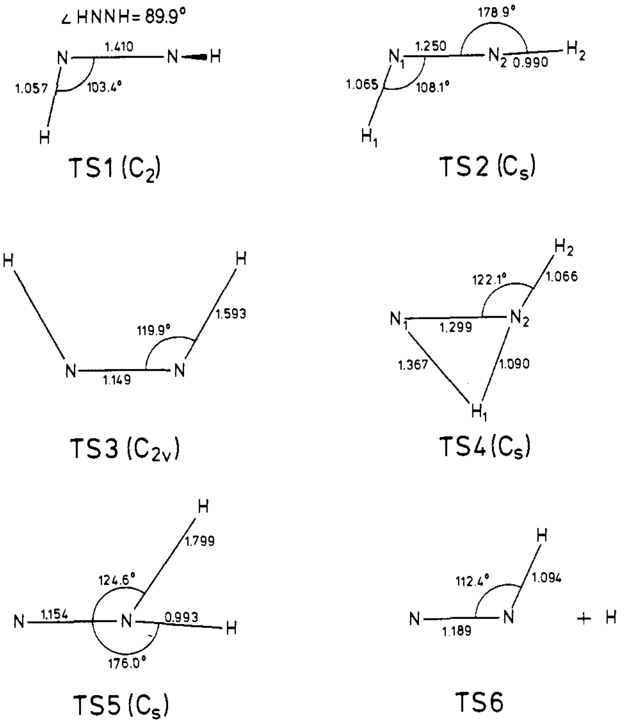
the values of the constants. For this reason we decided to compare our numbers with the more recent although less complete force fields of Craig and Levin.[4]

Based on the calculated ab initio force constants, we may derive a *complete* empirical force field by scaling the calculated force constants to the observed frequencies as described by Pulay et al.,[30] who do not scale the coupling constants independently. Rather if the diagonal constants f_{ii} and f_{jj} are scaled by C_i and C_j, then the coupling constant f_{ij} is scaled by $(C_iC_j)^{1/2}$. This simple empirically based procedure has worked well in a large number of cases.[30] In our case it allows us to obtain accurate force fields with only four parameters fitted to the six fundamental frequencies of either HNNH or DNND. These scaled quantum mechanical (SQM) force fields (or alternatively ab initio constrained empirical force fields) are also listed in Table III. The resulting scaled force fields are quite accurate, reproducing the experimental frequencies with an average deviation of 10.0 cm^{-1} (scaled to HNNH frequencies) and 8.2 cm^{-1} (scaled to DNND frequencies). This may be compared with the unscaled ab initio force field which reproduces these spectra with average deviations 51 cm^{-1} (HNNH) and 30 cm^{-1} (DNND). In fact, the four-parameter SQM force fields are almost as successful as the force fields of Craig and Levin[4] in reproducing the experimental frequencies. The force fields of Craig and Levin reproduce the frequencies of HNNH, HNND, and DNND with average deviations 5.7 cm^{-1} (eight-parameter field) and 6.6 cm^{-1} (seven-parameter field). The SQM force fields are based on a complete set of internal force constants and are determined from a smaller set of fitted parameters. We therefore believe that the SQM force fields are more accurate than the force fields of Craig and Levin.

Since only four parameters are needed to refine the SQM force fields, separate force fields are calculated for HNNH and DNND. The differences between these force fields reflect the anharmonicity of the energy surface. Following the discussion above, the DNND-scaled field is the most accurate *harmonic* force field, although an average of the HNNH- and DNND-scaled force fields may be determined that reproduces more accurately the observed anharmonic frequencies of the different modifications HNNH, HNND, and DNND.

Having compared the calculated vibrational fundamentals and force constants for *trans*-diazene with the available experimental data, we may consider the vibrational structures of the more elusive compounds *cis*- and isodiazene. In Table IV the calculated force field of *cis*-diazene is compared with the predicted force field of Craig and Levin,[4] and in Table V the calculated and predicted vibrational frequencies of *cis*-diazene are listed together with their corresponding double harmonic infrared intensities.

The force field of Craig and Levin[4] has been obtained by transferring force constants from the *trans*-diazene and the *cis*- and *trans*-methyldiazene molecules. From this force field, Craig and Levin predict that in *cis*-diazene the NH stretching modes are below 3000 cm^{-1} and the ND stretching modes are below 2200 cm^{-1}. These predictions are not supported by our calculations. Our calculations do indicate a lowering of NH and ND stretching modes due to a weakening of the NH bond. However, the force constant f_r is only reduced from 5.61 to 5.37 mdyn/Å, much less than the reduction from 5.39 (5.42) to 4.89 mdyn/Å predicted by Craig and Levin. Hence it appears that the assignments of Rosengren and Pimentel[3] (NH stretching at 3075 cm^{-1}) and later Wiberg et al.[31] (NH stretchings at 3116 and 3025 cm^{-1}) may be correct. We also note that in going from *trans*- to *cis*-diazene, there is a change in sign of the coupling between the NH stretching modes, which is reflected in the fact that in *cis*-diazene the symmetric stretching is significantly higher than the antisymmetric stretching.



TS1 (C_2) TS2 (C_s)

TS3 (C_{2v}) TS4 (C_s)

TS5 (C_s) TS6

Figure 2. Transition-state structures calculated on the diazene ground-state potential energy surface.

In accordance with Craig and Levin we conclude that while in *trans*-diazene the symmetric NH and ND bending modes are considerably higher than the corresponding antisymmetric modes, in *cis*-diazene the situation is reversed and the symmetric bending modes are *lower* than the antisymmetric modes. The splitting appears to be almost the same in both isomers (200 and 260 cm^{-1} in cis and 289 and 268 cm^{-1} in trans). Craig and Levin predicts a smaller splitting in *cis*-diazene.

In *cis*-diazene the NN stretching mode is higher than the symmetric bending modes (in HNNH and DNND), not lower as in *trans*-diazene. This is in accordance with the prediction of Craig and Levin. Finally the torsional mode of *cis*-diazene appears to be approximately 50 cm^{-1} lower than the corresponding mode in *trans*-diazene.

The slight distortion of isodiazene from C_{2v} symmetry has a quite drastic effect on the calculated force constants (Table VI) and frequencies (Table VII). Although this may be an artifact of the calculations due to inadequate treatment of electronic correlation effects, we report the force constants, frequencies, and infrared intensities since experimental data may be compared with the calculated numbers and hence easily refute or confirm the distorted model of isodiazene. For example, the NH stretching bands are separated by as much as 385 cm^{-1}, mainly because of the large difference between the NH stretching constants for the tight bond (5.885 mdyn/Å) and the loose bond (4.65 mdyn/Å). [See Note Added in Proof.]

The only available experimental data for isodiazene is the recent assignment of Sylwester and Dervan[6] of the NN stretching to 1574 cm^{-1} which is significantly higher than the corresponding observed frequency in *trans*-diazene (1529 cm^{-1}). This is in accord with our calculations (calculated frequencies 1611 and 1526 cm^{-1}, respectively), although the calculated difference is considerably larger than the observed difference.

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Table V. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for *cis*-Diazene[a]

	HNNH					DNND					HNND			
	calcd freq	emp freq	calcd intens	mode		calcd freq	emp freq	calcd intens	mode		calcd freq	emp freq	calcd intens	mode
A_1	3144	2966	47	NH str	A_1	2301	2178	26	ND str	A′	3110	2975	68	NH str
	1535	1558	2.6	NN str		1519	1543	1.9	NN str		2274	2183	37	ND str
	1416	1390	0.1	NH bd		1011	988	0.0	ND bd		1560	1415	29	NH bd
A_2	1267	1259	0	torsion	A_2	962	949	0	torsion		1512	1552	9.1	NN str
B_1	3074	2984	90	NH str	B_1	2249	2188	46	ND str		1114	1056	2.6	ND bd
	1616	1439	57	NH bd		1271	1124	21	ND bd	A″	1125	1115	12	torsion

[a] Empirical frequencies from Craig and Levin, ref 4.

Table VI. Valence Force Constants for Isodiazene[a]

f_R	11.66		
f_r	5.885	$f_{r'}$	4.605
f_α	1.489	$f_{\alpha'}$	1.469
f_γ	0.912		
f_{Rr}	1.106	$f_{Rr'}$	1.073
$f_{R\alpha}$	0.591	$f_{R\alpha'}$	0.594
$f_{rr'}$	0.358		
$f_{r\alpha}$	−0.248	$f_{r\alpha'}$	−0.187
$f_{r'\alpha}$	−0.225	$f_{r'\alpha'}$	−0.263
$f_{\alpha\alpha'}$	0.579		

[a] Units are mdyn/Å for stretching, mdyn Å for bending, and mdyn for stretch–bend interactions.

Table VII. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Isodiazene

	calcd freq	calcd intens	mode
A′	3253	157	NH str
	2868	238	NH str
	1814	5.7	scissoring
	1611	40	NN str
	1375	9.2	rocking
A″	1039	104	out-of-plane bending

IV. Transition Structures

The walks initiated at the equilibrium structures of diazene in Figure 1 resulted in the determination of six transition states. In Figure 2 we give the geometries of these transition states, and in Table I the total energies, the zero-point vibrational corrections, and the enthalpies at 0 K relative to $N_2 + H_2$ are reported. The zero-point vibrational corrections are determined from the harmonic frequencies given in Table VIII.

In all walks we used a Cartesian coordinate system without mass scaling. Initially we describe the walks from the *trans*-diazene equilibrium structure. The walk initiated along the lowest coordinate (+1) (out-of-plane torsion) reached the transition structure TS1 in seven iterations. The (−1) walk gives the same transition structure as the (+1) walk by symmetry. The second Hessian eigenvalue represents an antisymmetric bend coordinate, and walks in the (+2) and (−2) directions are therefore identical. The (+2) walk took 11 iterations to reach TS2. The third coordinate is symmetric and the (+3) walk resulted in dissociation (TS6) with the hydrogen atom leaving at about the same angle as in *trans*-diazene. The walk was an uphill movement all the way until the dissociation was completed. The (−3) walk and all higher mode walks did not lead to transition structures as Hessian structures were encountered that cannot be handled by the algorithm.

For *cis*-diazene the lowest Hessian eigenvalue represents a symmetric bend coordinate. In the (+1) walk TS3 was encountered after a long walk of 14 iterations. The (−1) walk resulted in the transition structure TS2. Mode 2 represents the out-of-plane torsion and resulted as expected in transition structure TS1. Mode 3 represents an antisymmetric bend and gave dissociation to TS6 with the hydrogen atom leaving at about the same angle as in *cis*-diazene. Hessian eigenvalue number four represents a symmetric stretch coordinate and the (+4) walk gave TS3 in eight iterations.

For isodiazene the (+1) walk resulted in dissociation (TS6), while the (−1) walk gave transition state TS4 in eight iterations. Hessian eigenvalue number 2 is an out-of-plane bending mode, and walks along this mode (±2) resulted also in the planar TS4 transition structure for this path after 15 iterations. It should be noted that the transition structure determined in the (−1) walk differs slightly from the transition structure obtained in the (±2)

Table VIII. Transition-State Frequencies[a]

TS1 (C_2)[a]		TS2 (C_s)		TS3 (C_{2v})		TS4 (C_s)		TS5 (C_s)		TS6 (C_s)	
A	3323*i*	A′	3957	A_1	1974*i*	A′	3082	A′	3831	A′	2247
	2991		2876		1925		2625		2387*i*		1614
	1257		2075*i*		744		2186*i*		1892		1141
	923		1614	A_2	518		1513		1240		
B	3001		1536	B_2	817		1330		742		
	1279	A″	684		258	A″	574	A″	713		

[a] Units are cm^{-1}.

Table IX. Transition States Optimized with a Correlated Wave Function (distances in Å)

TS1		Schmidt Gordon[18]	TS2		Parsons Dykstra[8]	TS3		Brandemark Siegbahn[9]
r_{NN}	1.410	1.436	r_{NN}	1.250	1.286	r_{NN}	1.149	1.185
r_{NH}	1.057	1.027	$r_{N_1H_1}$	1.065	1.040	r_{NH}	1.593	1.635
θ_{NNH}	103.4°	103.5°	$r_{N_2H_2}$	0.990	0.993	θ_{NNH}	119.9°	121.5°
∠HNNH	89.9°	90.1°	$\theta_{H_1N_1N_2}$	108.1°	109.0°			
			$\theta_{H_2N_2N_1}$	178.9°	177.8°			

TS4		Parsons Dykstra[8]	TS6		Brandemark Siegbahn[8]	Casewit Goddard[10]
r_{NN}	1.299	1.286	r_{NN}	1.189	1.190	1.209
$r_{N_2H_1}$	1.090	1.032	r_{NH}	1.094	1.079	1.053
$r_{N_2H_2}$	1.066	1.040	θ_{NNH}	112.4°	113.2°	114.6°
$\theta_{N_1N2H_2}$	122.1°	121.2°				
$\theta_{N_1N_2H_1}$	69.2°	77.5°				

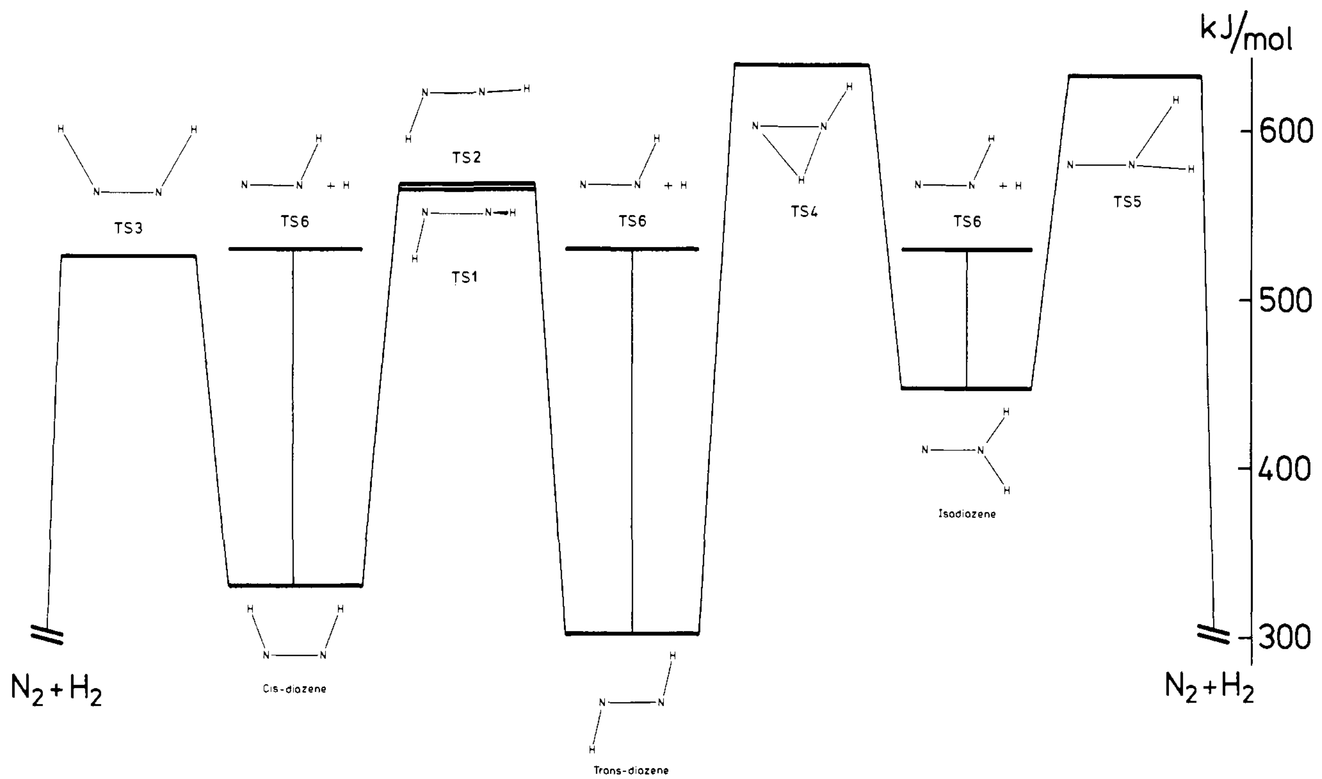

Figure 3. Diagram illustrating the activation energies for various reactions on the diazene ground-state potential energy surface.

walk which is the one referred to in Table I and Figure 2. In the (−1) walk $r_{N_2H_2}$ is 1.034 Å and $r_{N_2H_1}$ is 1.108 Å with all other distances less than 0.001 Å from the ones in Figure 2. The different transition structures which result from the (−1) and the (±2) walks represent different minima on the MCSCF energy hypersurface. The existence of several minima on an MCSCF energy hypersurface is one of the major problems in using a highly constrained CAS MCSCF wave function to determine total energies.[32]

Most of the transition structures in Figure 2 have been described in previous calculations. In Table IX we report the ones that have been calculated with correlated wave functions. The basis sets in the calculations in Table IX are of very similar quality. Schmidt and Gordon[18] used MCSCF with four electrons in four active orbitals to determine TS1. The geometry they obtain is very similar to the one we determine with eight electrons in eight active orbitals. TS2 and TS4 have been determined in SCEP calculations[8] which gave geometries very similar to ours. The major difference is that in TS4 Parsons and Dykstra[8] find shorter $r_{N_2H_2}$ and $r_{N_2H_1}$ bond lengths. The transition structures TS3 and TS6 of Brandemark and Siegbahn[9] have been determined in MCSCF calculations with the same active space. Brandemark and Siegbahn's TS3 calculation did not contain polarization functions which is the reason for the discrepancies with our calculation. Brandemark and Siegbahn used a triple-ζ basis with polarization functions to determine TS6, and our results are very similar to theirs. The TS6 structure by Casewit and Goddard[10] was optimized using a GVB wave function and is slightly different from ours.

It is worth noticing for TS6 that the diazenyl radical has a transition state (r_{NN} = 1.158 Å, r_{NH} = 1.251 Å, and θ_{NNH} = 113.6°) with a barrier only 5.4 kJ/mol above the minimum.[21] After the zero-point vibrational correction has been added, the diazenyl radical becomes unstable with a total energy at the minimum being 6.8 kJ/mol higher than the total energy at the transition state. The harmonic frequencies which are used to correct for zero-point vibrations at the transition state are (in cm^{-1}) 1962, 1656i, and 1013.

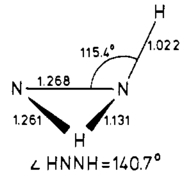

Figure 4. The transition state for the isodiazene ↔ *trans*-diazene isomerization from the Hartree–Fock calculation of Ito and Nagase.[11]

In Figure 3 we display the activation energies that are required in the various reactions on the ground-state potential energy surface.

The pathways for the unimolecular shift of hydrogen in the *cis*-diazene ↔ *trans*-diazene and in the isodiazene ↔ *trans*-diazene rearrangement reactions have previously been extensively studied. For the *cis*-diazene ↔ *trans*-diazene isomerization recent investigations have unanimously claimed that the hydrogen shift goes through inversion at one of the nitrogen atoms rather than through internal rotation around the N=N bond.[8,10,16,19] This conclusion is based on a rather crude optimization of the rotation barrier using a two-configuration MCSCF wave function.[19] This gives a rotation barrier which is much higher than the barrier for inversion. The geometry of the two-configuration rotation transition state is r_{NN} = 1.247 Å, r_{NH} = 1.019 Å, θ_{NNH} = 127°, and ∠HNNH = 90°. A comparison with the optimized transition structure TS1 in Figure 2 shows clearly that this geometry has little similarity with the transition structure we determine. We find that the rotation and inversion barriers after zero-point vibrational corrections only differ by 1.8 kJ/mol (see Table I), the rotation barrier being the smaller. The dissociation pathway TS6 was ruled out by Casewit and Goddard based on GVB calculations optimizing only the TS6 transition structure. After zero-point vibrational corrections we find that the dissociation pathway is substantially lower (see Figure 3 and Table I) than the rotation and inversion barriers. However, recombination after dissociation is unlikely as the diazenyl radical was found to be unstable.

Pople et al.[16] and Ito and Nagase[11] have both investigated the isodiazene ↔ *trans*-diazene isomerization using an SCF wave function. They both find an out-of-plane transition structure. In Figure 4 we have displayed the transition structure given by Ito

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[32] Golab, J.; Yeager, D. L.; Jørgensen, P. *Chem. Phys.* **1984**, *93*, 83.

and Nagase. Both Pople et al. and Ito and Nagase report that if planar C_s symmetry is imposed during the optimization, a stationary point is determined similar to TS4 but with a Hessian having two negative eigenvalues. Pople et al. carried out single-point calculations with correlation at the two stationary points they have determined, and found a lower barrier for the in-plane structure than for the out-of-plane structure. Pople et al. then conclude that the isodiazene ↔ *trans*-diazene isomerization goes through a planar transition structure. Ito and Nagase also carried out single-point calculations using third-order Møller–Plesset (MP3) perturbation theory. They did not find such a significant lowering of the total energy for the planar structure as reported by Pople et al.

Our calculations show that when correlation is included in the optimization of the geometry, the out-of-plane transition structure in Figure 4 becomes planar. The (±2) walks toward TS4 passed right through the region of the Hartree–Fock transition structure in Figure 4. The out-of-plane transition structure in Hartree–Fock is, therefore, an artifact of using a wave function that is not flexible enough to reliably describe the hydrogen shift.

The dissociation pathway TS6 has been found by several authors[10,13] to have a significantly lower barrier than the in-plane reaction pathway. Our calculations are in agreement with this conclusion (see Figure 3). However, we recall that recombination is unlikely as the diazenyl radical was found to be unstable. It is worth noticing that the walks which started out from the *trans*-diazene equilibrium structure did not find the transition structure TS4 as bifurcations were encountered during the walk. There is not a single valley without branches connecting *trans*-diazene with TS4.

In Table VIII we have reported the harmonic frequencies for the transition structures in Figure 2. As is clear from Table VIII the imaginary frequencies (representing the negative curvature direction) are larger than normally observed, indicating that tunneling is likely to be the preferred unimolecular rearrangement pathway. This is particularly true for the *cis*-diazene ↔ *trans*-diazene isomerization where the rotation barrier (TS1) has an extremely high imaginary frequency of 3323*i*, which strongly favors tunneling.

Based on the Woodward–Hoffmann rules[33] the formation of *cis*-diazene from $N_2 + H_2$ is symmetry forbidden with conservation of C_{2v} symmetry, while the formation of *trans*-diazene is symmetry allowed with conservation of C_2 symmetry. We have tried unsuccessfully to locate structures representing the Woodward–Hoffmann transition structures. To do this we have carried out walks where $N_2 + H_2$ are approaching each other. We have found that breaking symmetry becomes energetically favorable. The Woodward–Hoffmann rules can for that reason not be applied to the formation of diazene. The transition structure TS5 from isodiazene is the only transition state we have found that dissociates into $N_2 + H_2$ fragments.

Finally we want to mention that TS3 has a geometrical structure that makes it important in the stereospecific hydrogenation of nonpolar bonds.

V. Discussion

As a model to give a uniform description of the ground-state potential energy surface of diazene, we have used a CAS MCSCF wave function with eight electrons in eight orbitals and a split-valence plus polarization basis. We have determined the three equilibrium structures of diazene and the reaction paths leading to a total of six transition structures. In particular, we have analyzed the reaction pathways for the unimolecular shift of hydrogen in the *cis*-diazene ↔ *trans*-diazene and in the isodiazene ↔ *trans*-diazene isomerization reactions. Our calculations demonstrate the importance of using a consistent and fairly accurate model for examining all the possible pathways for the reaction. In previous investigations of the *cis*-diazene ↔ *trans*-diazene isomerization, the transition structure for inversion at one nitrogen atom (TS2 in Figure 2) and for rotation around the N=N bond (TS1) have been determined with wave functions of different quality, and consequently the inversion has been assumed to have a much lower barrier.[8,10,16,19] Our calculations indicate that the barriers for inversion and rotation are very similar. The rotation barrier is much narrower, suggesting rotation to be the most likely mechanism (via tunneling).

For the isodiazene ↔ *trans*-diazene isomerization we have showed that the SCF model is unable to give an even qualitatively correct description of the reaction path. The out-of-plane transition structure, which is the one obtained at the Hartree–Fock level[11,16] (see Figure 4), becomes planar as correlation is considered in the structure optimization. This example clearly shows that the Hartree–Fock model can only be used with extreme care to study reaction paths on potential energy surfaces.

We have calculated the vibrational frequencies for *trans*-diazene and constructed the hitherto most accurate valence force field for *trans*-diazene. Supported by the good agreement for *trans*-diazene we predict the *cis*-diazene spectrum and contest another recent prediction.[4]

The comparison of our calculated electronic structure data and experimental and previously calculated data shows that the model we are using gives a uniform semiquantitatively to quantitatively correct description of the diazene ground-state potential surface. The model describes equally reliably equilibrium structure data, reaction paths, and transition structure geometries. Small differences in the activation energies of different reaction paths can, of course, not be trusted in this model. To get such reliability requires that calculations are carried out with a larger basis and especially with an extended active space where the 2s orbital on nitrogen is included in the active space. In such calculations the stationary-point geometries of the presented calculations can, of course, be used as initial guesses in the search for stationary points of the larger calculations. With our present computational facilities we are unable to carry out such accurate calculations.

Note Added in Proof. To investigate whether or not the distorted equilibrium structure of isodiazene is an artifact of our calculations, we have carried out a calculation at the optimized geometry in Figure 1 using an MCSCF wave function constructed by distributing twelve electrons in twelve orbitals (2s and 2p on nitrogen included). The MCSCF energy at this geometry is −109.908299 au and the norm of the molecular gradient is 0.0275 au. The Newton step calculated from the molecular gradient and Hessian indicates that at this level of approximation the equilibrium geometry of isodiazene has C_{2v} symmetry with $r_{NH} = 1.038$ Å, $r_{NN} = 1.224$ Å, and $\theta_{NNH} = 124.4°$. We estimate the uncertainties in these numbers to be 0.002 Å for the bond lengths and 0.4° for the bond angle.

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(33) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstrasse, 1970.