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Substituent Effects and the Cis-Trans Isomerization of Diazenes

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Abstract: We have performed ab initio calculations on substituted diazenes, $R-N=N-R'$ where R and R' can be $-H$, $-CH_3$, $-F$, and $-CN$. The geometry optimized calculations favored the trans geometry by about 6 kcal/mol when neither R nor R' is F . When there is a single F substituent, the trans is favored by about 1 kcal/mol. With $R = R' = F$, the cis is slightly preferred. An electronegativity argument is offered for these trends based on the observation that the substituents are more negative in the cis geometry than in the trans. The mechanism of the cis-trans interconversion was investigated. In all cases the inversion mechanism was found to be of lower energy than was the rotation mechanism. The activation energy was found to vary with the π -electron accepting ability of the inverting group in the order $F > H > CH_3 > CN$. When R was H and R' was NO_2 or CHO , the isomerization pathway is calculated to be one which involves both an inverting motion and a rotation about the $N-NO_2$ or $N-CHO$ bond so as to maximize the stabilization obtained through conjugative interactions. When R was H and R' was NH_2 , the opposite results are obtained. The effect of interaction between the R and R' substituents on the activation energy was studied. If the noninverting substituent is an efficient electron withdrawer, a decrease in the activation energy was calculated.

There has been a substantial and sustained interest in the interactions between lone pairs and substituents. At one level these investigations concern the height of the inversion barrier for substituted ammonias, where it has been established, both theoretically and experimentally, that the choice of substituents can have a sizable effect.¹ For example, the inversion barrier of NH_2F is calculated² to be 20.3 kcal/mol (an experimental value³ for difluoroamines is greater than 18 kcal/mol) while that of NH_2CN is calculated² to be 1.8 kcal/mol (experimentally⁴ 1.9). Of particular experimental importance have been the cyclic aziridine systems. Andose, Lehn, Mislow, and Wagner observed⁵ a correlation of inversion rates with the Hammett σ^- constants for a variety of meta- and para-substituted *N*-phenyl-2,2-dimethylaziridines.

Substituent effects have also been of interest on doubly bonded nitrogen systems. The parent systems most studied have been the diazene⁶⁻³⁹ ($HN=NH$) methylenimide^{30,40-55} ($H_2C=NH$), and carbodiimide^{28,56,57} ($HN=C=NH$).⁵⁸ The three systems are similar to each other and conclusions reached for one are most likely applicable to the others. Most of the ab initio theoretical studies of the diazene system have centered on the N_2H_2 molecule.²⁸⁻³⁹ It is worthwhile noting that substitutional effects have been systematically examined in the theoretical spectral studies of Ditchfield, Del Bene, and Pople³⁶ for the (n,π^*) excitation as well as that of Radom, Hehre, and Pople.³⁴

In the present paper we describe the application of ab initio, geometry optimized calculations to a study of substitu-

ent effects on the singlet ground-state properties of diazenes. In particular we are concerned with (a) the cis-trans energy difference, (b) the effect of substituents on the energetics of the cis-trans isomerization pathway (see Scheme I), and (c) the interaction of the inverting and non-inverting substituents in the equilibrium and transition state geometries.

Calculations

The ab initio calculations were performed using a minimal STO-3G basis set^{63a} with the GAUSSIAN-70 program.⁶⁴ In a few cases the results were checked by using an extended STO4-31G basis set.^{63b}

The geometries were optimized subject to the following constraints: for methyl groups, C-H was kept at 1.09 Å and the HCH angle at 109.47°; the N-C≡N linkage was kept at 180°. The method of optimization consisted of successively optimizing one geometric parameter after another with the aid of parabolic fitting. At least two cycles, where in each parameter was optimized, were performed for each molecule. Our estimate is that bond lengths are optimized to ± 0.002 Å and bond angles to $\pm 1^\circ$.

Overall Results

The calculated energies and Mulliken populations of the optimized cis and trans isomers as well as some transition states for each molecule ($R-N=N-R$) studied are presented in Table I. Several trends may be immediately noticed. The $N1-N2$ overlap population is always higher in

Table I. Calculated Characteristics of the Diazene Molecules Studied. Values Are Reported for the Cis and Trans Isomers and the Inversion Transition State

R—N1=N2=R' ^a	E, hartrees	Mulliken population analysis							
		Gross charges		R		Overlap populations			
		N1	N2		R'	N1=N2	R	R'	
FN=NF									
Cis	-303.44098	0.041	0.041	F: -0.041	F: -0.041	0.752	FN: 0.336	NF: 0.336	
Trans	-303.44085	0.032	0.032	F: -0.032	F: -0.032	0.742	FN: 0.345	NF: 0.345	
Invts	-303.30752	0.102	-0.098	F: -0.101	F: 0.097	0.815	FN: 0.305	NF: 0.344	
HN=NH									
Cis	-108.54524	-0.142	-0.142	H: 0.142	H: 0.142	0.834	HN: 0.587	NH: 0.587	
Trans	-108.55695	-0.161	-0.161	H: 0.161	H: 0.161	0.828	HN: 0.595	NH: 0.595	
Invts	-108.45113	-0.100	-0.285	H: 0.107	H: 0.279	0.895	HN: 0.550	NH: 0.712	
H₃CN=NCH₃^b									
Cis	-185.71566	-0.108	-0.108	C: -0.128	C: -0.128	0.824	CN: 0.562	NC: 0.562	
				H: 0.079	H: 0.079		CH: 0.761	CH: 0.761	
Trans	-185.72651	-0.122	-0.122	C: -0.114	C: -0.114	0.820	CN: 0.573	NC: 0.573	
				H: 0.079	H: 0.079		CH: 0.762	CH: 0.762	
Invts	-185.62834	-0.063	-0.222	C: -0.133	C: -0.046	0.881	CN: 0.515	NC: 0.695	
				H: 0.062	H: 0.093		CH: 0.759	CH: 0.762	
N3CN=NCN4									
Cis	-289.61199	-0.022	-0.022	C: 0.138	C: 0.138	0.808	CN1: 0.632	N2C: 0.632	
				N3: -0.116	N4: -0.116		N3C: 1.424	CN4: 1.424	
Trans	-289.62258	-0.035	-0.035	C: 0.161	C: 0.061	0.798	CN1: 0.648	N2C: 0.648	
				N3: -0.127	N4: -0.127		N3C: 1.429	CN4: 1.429	
Invts	-289.54988	0.024	-0.119	C: 0.135	C: 0.226	0.882	CN1: 0.586	N2C: 0.938	
				N3: -0.144	N4: -0.123		N3C: 1.427	CN4: 1.322	
FNNH									
Cis	-206.00282	0.056	-0.154	F: -0.074	H: 0.172	0.812	FN: 0.333	NH: 0.585	
Trans	-206.00449	0.039	-0.169	F: -0.056	H: 0.186	0.794	FN: 0.340	NH: 0.606	
R' Invts	-205.91906	0.097	-0.281	F: -0.112	H: 0.297	0.927	FN: 0.306	NH: 0.707	
R Invts	-205.84244	-0.103	-0.095	F: 0.079	H: 0.119	0.780	FN: 0.349	NH: 0.548	
FNNCH₃^b									
Cis	-244.58739	0.036	-0.109	F: -0.082	C: -0.120	0.802	FN: 0.329	NC: 0.571	
					H: 0.092			CH: 0.762	
Trans	-244.58935	0.019	-0.117	F: -0.063	C: -0.109	0.792	FN: 0.340	NC: 0.581	
					H: 0.090			CH: 0.763	
R' Invts	-244.51047	0.069	-0.212	F: -0.122	C: -0.042	0.909	FN: 0.302	NC: 0.677	
					H: 0.103			CH: 0.764	
R Invts	-244.42843	-0.115	-0.039	F: 0.075	C: -0.131	0.784	FN: 0.348	NC: 0.514	
					H: 0.070			CH: 0.760	
FN=NCN3									
Cis	-296.53410	0.106	-0.077	F: -0.035	C: 0.142	0.788	FN: 0.340	N2C: 0.633	
					N3: -0.135			CN3: 1.426	
Trans	-296.53654	0.095	-0.089	F: -0.023	C: 0.159	0.770	FN: 0.350	N2C: 0.656	
					N3: -0.141			CN3: 1.431	
R' Invts	-296.47343	0.142	-0.169	F: -0.056	C: 0.227	0.886	FN: 0.324	N2C: 0.910	
					N3: -0.144			CN3: 1.351	
R Invts	-296.38328	-0.046	0.008	F: 0.114	C: 0.105	0.794	FN: 0.345	N2C: 0.524	
					N3: -0.180			CN3: 1.429	
HN=NCH₃^b									
Cis	-147.13386	-0.155	-0.092	H: 0.131	C: -0.129	0.834	HN: 0.578	NC: 0.565	
					H: 0.082			CH: 0.760	
Trans	-147.14211	-0.178	-0.106	H: 0.156	C: -0.115	0.822	HN: 0.598	NC: 0.569	
					H: 0.081			CH: 0.762	
R' Invts	-147.04262	-0.123	-0.214	H: 0.099	C: -0.046	0.877	HN: 0.547	NC: 0.693	
					H: 0.097			CH: 0.764	
R Invts	-147.03732	-0.295	-0.043	H: 0.275	C: -0.132	0.898	HN: 0.713	NC: 0.517	
					H: 0.065			CH: 0.759	
HN=NCN3									
Cis	-199.08339	-0.094	-0.058	H: 0.180	C: 0.123	0.818	HN: 0.590	N2C: 0.616	
					N3: -0.151			CN3: 1.427	
Trans	-199.09307	-0.109	-0.077	H: 0.195	C: 0.148	0.810	HN: 0.601	N2C: 0.627	
					N3: -0.157			CN3: 1.433	
R' Invts	-199.01757	-0.058	-0.158	H: 0.167	C: 0.209	0.874	HN: 0.577	N2C: 0.946	
					N3: -0.160			CN3: 1.322	
R Invts	-198.99523	-0.229	0.005	H: 0.313	C: 0.101	0.916	HN: 0.702	N2C: 0.519	
					N3: -0.190			CN3: 1.429	
H₃CN=NCN3^b									
Cis	-237.67197	-0.048	-0.078	C: -0.126	C: 0.120	0.817	CN1: 0.569	N2C: 0.603	
				H: 0.099	N3: -0.165		HC: 0.761	CN3: 1.426	
Trans	-237.68075	-0.057	-0.097	C: -0.111	C: 0.146	0.804	CN1: 0.576	N2C: 0.631	
				H: 0.096	N3: -0.169		HC: 0.762	CN3: 1.432	
R' Invts	-237.60598	-0.005	-0.174	C: -0.120	C: 0.206	0.874	CN1: 0.546	N2C: 0.947	
				H: 0.088	N3: -0.173		HC: 0.761	CN3: 1.323	
R Invts	-237.58966	-0.162	-0.020	C: -0.043	C: 0.093	0.897	CN1: 0.668	N2C: 0.509	
				H: 0.111	N3: -0.202		HC: 0.763	CN3: 1.428	

Table I (Continued)

R—N1=N2=R' ^a	Mulliken population analysis								
	E, hartrees	Gross charges		R	R'	Overlap populations			
		N1	N2			N1=N2	R	R'	
HN=NC(H)O									
Cis	-219.78472	-0.138	-0.121	H: 0.165	C: 0.196 H: 0.093 O: -0.196	0.830	HN: 0.573	NC: 0.534 CH: 0.744 CO: 0.892	
Trans	-219.78837	-0.158	-0.124	H: 0.170	C: 0.208 H: 0.080 O: -0.176	0.813	HN: 0.599	NC: 0.559 CH: 0.729 CO: 0.903	
Invts	-219.71803	-0.090	-0.184	H: 0.147	C: 0.275 H: 0.094 O: -0.241	0.883	HN: 0.567	NC: 0.698 CH: 0.751 CO: 0.873	
HN=N—N3(O1)O2 ^c									
Cis	-309.27022	-0.145	0.015	H: 0.254	N3: 0.166 O1: -0.213 O2: -0.079	0.889	HN: 0.464	N2N3: 0.267 N3O1: 0.518 N3O2: 0.607	
Trans ^d	-309.25595	-0.115	0.005	H: 0.211	N3: 0.198 O1: -0.153 O2: -0.147	0.823	HN: 0.604	N2N3: 0.379 N3O1: 0.538 N3O2: 0.548	
Invts	-309.13862	-0.050	-0.096	H: 0.169	N3: 0.284 O1: -0.153 O2: -0.153	0.842	HN: 0.566	N2N3: 0.539 N3O1: 0.506 N3O2: 0.506	
HN=N—N3H ₂									
Cis	-162.87005	-0.173	-0.005	H: 0.136	N3: -0.316 H: 0.179	0.833	HN: 0.582	N2N3: 0.526 N3H: 0.659	
Trans	-162.87753	-0.201	-0.022	H: 0.162	N3: -0.309 H: 0.185	0.816	HN: 0.607	N2N3: 0.543 N3H: 0.665	
Invts	-162.75875	-0.145	-0.125	H: 0.098	N3: -0.239 H: 0.205	0.804	HN: 0.554	N2N3: 0.707 N3H: 0.682	

^a Invts refers to the estimated transition state for the inversion pathway. The NNR' angle is 180° except for R' = NO₂ where it is 170° and the HNNN dihedral angle is 90°. ^b Values are averaged over the substituent hydrogens. ^c O1 is the cisoid or syn oxygen. O2 is transoid or anti. ^d The dihedral angle H—N=N—NO₂ optimized to 23°.

the cis isomer than in the trans. The difference usually being about 0.010.

The optimized bond N1-N2 bond lengths follow the same trend—the bond in the cis isomer usually being about 0.007 Å shorter than in the trans. In general, the N-N-R angles are larger in the cis isomer than in the trans. This phenomenon is probably simply related to the steric repulsion between R and R'. The larger angle increases the amount of nitrogen 2s orbital participation in the N-R or N-R' bond. Another persistent trend is that the diazene nitrogen atoms are more negative in the trans isomers than in the cis.

The cis,trans energy difference, $\Delta E_{t-c} = E_{trans} - E_{cis}$, is quite constant for the set of substituents H, Me, and CN at -0.009 to -0.012 hartree as shown in Table II. Interestingly ΔE_{t-c} is slightly larger if R = R' than if R ≠ R'. When R = F and R' = H, Me, or CN, the value of ΔE_{t-c} becomes smaller having a value of about -0.002 hartree. Furthermore with R = R' = F, the cis isomer is preferred to the trans in agreement with experimental data.⁶⁵

We now attempt to investigate why the presence of a fluorine substituent lowers the energy of the cis isomer more than it does the energy of the trans isomer. A priori one might expect that the effect could be due either to the fluorine's lone pairs or to its high electronegativity.

There have been several studies⁶⁶⁻⁷⁸ which have focused on the importance of nonbonded interaction involving lone pairs. Epitotis⁷⁹ has discussed "attractive nonbonded interactions" between halogen lone pairs. Similar interactions seem to be important in rationalizing the conformations of N₂O₄ and B₂F₄.⁸⁰ Hoffmann⁸¹ has used related ideas in discussing "steric attractions" for highly exothermic reactions.

Radom, Hehre, and Pople⁷⁶ have examined the rotational potential of HOOF. Although the optimal HOOF dihedral

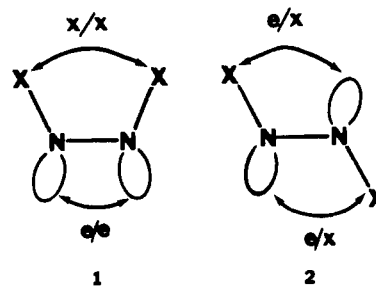
Table II. Energy Difference between the Cis and Trans Isomers of RNNR' Expressed in Hartrees^a

R'	R			
	H	CH ₃	CN	F
H	-0.01171	-0.00825	-0.00968	-0.00167
CH ₃		-0.1085	-0.00878	-0.00196
CN			-0.1059	-0.00244
F				+0.00013

^a Note: 1 hartree = 627.7 kcal/mol. The values reported were obtained from geometry optimized STO-3G calculations.

angle is found to be 75°, the cis planar structure is found to be of lower energy than the trans. The authors interpret this as being "consistent with the dipole interactions". In N₂F₂, however, such interactions should favor the trans form as opposed to the cis which is of lower energy, experimentally,⁶⁵ and in our calculations as well.

Wolfe⁷⁷ has discussed the interactions between lone pairs, *e*, and substituents, *X*. Examining the diazene system, we see that, in the cis isomer (1), there is a lone-pair/lone-pair interaction, *e/e*, and a substituent-bond/substituent-bond interaction, *X/X*. On the other hand, in trans form (2),



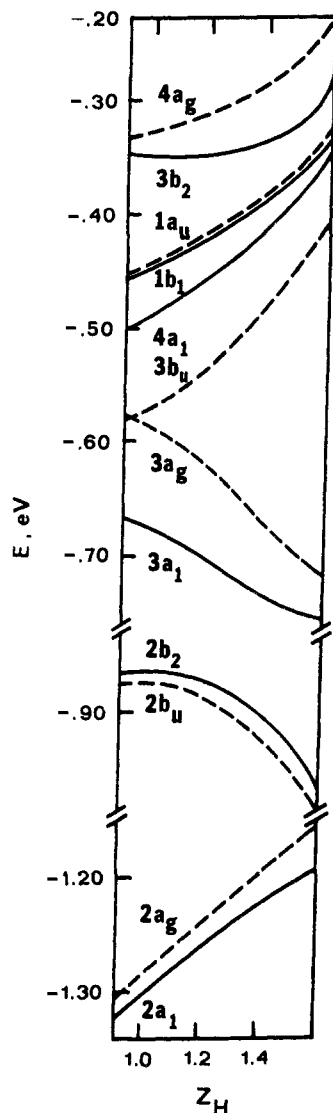


Figure 1. Variation in the STO-3G, valence shell molecular orbital energies of N_2H_2 with changes in the nuclear charges. As Z_H is increased, Z_N is simultaneously decreased. Dashed lines represent the trans isomer orbital energies and solid lines those of the cis isomer.

there are two lone pair/bond interactions, e/X . If these interactions were to be dominant, then the condition for the cis isomer having a lower energy would be given by eq 1.

$$(e/e + X/X) - 2(e/X) < 0 \quad (1)$$

Wolfe⁷⁷ arrived at the same expression during investigations of the gauche effect.

Before attempting to evaluate the applicability of the various interpretative schemes, it is useful to investigate the dependence of ΔE_{t-c} upon the electronegativity of the substituents. Toward this end we have performed calculations on the model compound N_2H_2 modifying the nuclear charges so as to mimic electronegativity effects.⁸² The procedure was to use an STO-3G basis set and add a fractional charge to the hydrogen nuclear charge (Z_H) while subtracting the same amount from the nitrogen nuclear charge. When the charge on the hydrogen nuclei was increased, the cis-trans energy gap decreased, finally favoring the cis form when the "hydrogen" nuclear charge (Z_H) was about 1.5 and that of the "nitrogens" was 6.5.

Figure 1 shows a plot of the orbital energies for the cis form (solid lines) and the trans form (dashed lines) as a function of Z_H , the hydrogen nuclear charge. The overall

behavior is qualitatively understood in terms of the charge distribution within each molecular orbital. The lowest lying molecular orbitals, $2a_1$ for trans and $2a_g$ for the cis isomer, are predominantly N-N σ bonding and thus rise in energy as Z_N decreases.

The next two sets of molecular orbitals are the antisymmetric and the symmetric combination of the N-H σ bonds. Due to the substantial density on the hydrogens, an increase in Z_H causes a decrease in the molecular orbital energies. The highest ($4a_g$ and $3b_2$) and the third from the highest ($4a_1$ and $3b_u$) occupied orbitals are nitrogen lone pairs and consequently go up in energy. The orbital set which is second from the top ($1a_u$ and $1b_2$) are the π orbitals located entirely on the nitrogens and consequently rise in energy.

Probably the most reliable information may be obtained by comparing the slopes of the curves at $Z_H = 1.0$. If the slope of the trans isomer is larger (more positive) than that of the cis isomer, then we assume that a preference for the cis form is introduced. The largest difference in the slopes is found in the set of highest occupied orbitals where the energy of the orbital of the trans isomer rises substantially faster than that of the cis. The coefficient of the hydrogen 1s atomic orbital in the cis molecular orbital is substantially greater (0.368) than that in the trans $3b_2$ orbital (0.286). Additionally, as shown in Table I, the substituents in the cis isomer are more negative than in the trans. As the substituents are made more electronegative, the difference in charges on the substituents becomes more important, and the cis isomer is lower in energy than the trans.

As had been noted before,⁸³ the ordering of the symmetry-adapted diazene lone pair combinations is reversed in the cis and trans isomers. In the cis isomer, the plus combination, orbital $4a_1$, is of lower energy than the minus combination, $3b_2$. In the trans isomer, the minus combination, orbital $3b_u$, is of lower energy than the plus combination, $4a_g$.

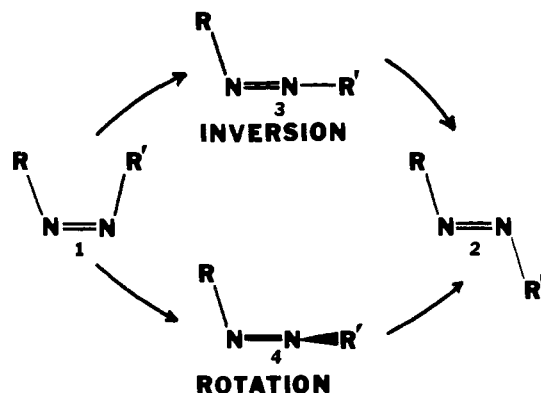
The results of these numerical experiments can be interpreted in different ways. We would expect that donation of the nitrogen lone pairs into the adjacent N-R σ^* orbital (hyperconjugation) would increase as the electronegativity of the R group is increased. If the donation is greater for the cis isomer than for trans and the difference increases as the electronegativity of the substituents increases, a rationale would be provided for the lower energy of cis N_2F_2 . In fact, examining the N-N π' overlap population (in the molecular plane but perpendicular to the internuclear axis) provides some support for this interpretation. Using a single geometry that represents an average of the optimized cis and trans N_2H_2 structures, the N-N π' overlap population with $Z_H = 1.0$ is -0.015 for the cis and -0.019 for the trans with a difference of 0.004. When Z_H is 1.2 the π' overlap populations become 0.020 for the cis and 0.008 for the trans with a difference of 0.012. Clearly hyperconjugative donation is present and the larger difference with the more electronegative substituents could argue in favor of such donation controlling the isomer stability. However, if we examine the total N-N overlap populations, we find that the difference between the cis and trans overlap population forms does not change substantially with Z_H . The total N-N overlap population ($Z_H = 1.0$) is 0.826 for the cis isomer and 0.838 for the trans giving a difference of 0.012. When Z_H is 1.2, the cis value is 0.929 and the trans yields 0.943 for a difference of 0.014. The change in the cis-trans difference is now quite small.

Furthermore, in examining the total N-N overlap populations of Table I, we find that the cis isomer consistently has a greater value than the trans. As before, this might suggest that hyperconjugation could be dominant. However, there is very little change in the difference of the cis and trans N-N overlap population for the various mole-

cules. The differences in the total N-N overlap populations for several molecules are: FNNF, 0.010; HNNH, 0.006; CH₃NNCH₃, 0.004; NCNNCN, 0.010; FNNH, 0.018; FNNCH₃, 0.010; FNNCN, 0.018; HNNCH₃, 0.012; HNNCN, 0.008; CH₃NNCN, 0.013. Although some of the fluorinated molecules show a larger N-N overlap population, we do not detect a clear correlation between the cis-trans energy difference and the total N-N overlap population. Consequently, we are hesitant to accept the idea of N1 (lone pair) → N2-R' (σ^*) donation as being the sole dominant factor in controlling the isomer stability. Rather, we prefer to ascribe a parallel role to electronegativity effects: fluorines prefer sites of high charge density (cis geometries). However, the origin of the higher charge density on the substituents in the cis isomer may well lie in hyperconjugative effects.

Let us put forth, however, another interpretation of these results, suggested, in part, to us by Professor M. J. S. Dewar of The University of Texas at Austin. As has been noted, the hyperconjugative interaction of the nitrogen lone pairs with the adjacent σ^* functions appears to be greater in the cis geometry than in the trans. This is evidenced by the greater total and in-plane π -type N-N overlap population. If we accept this as introducing a general preference for the cis isomer, then we are left with explaining the lower energy of the trans forms for substituents other than F. It is well known⁸⁴ that the hybridization of the lone pair in NX₃ compounds changes as a function of electronegativity of the X substituent, becoming higher in s character as the X electronegativity increases. Now consider the electrostatic repulsion of the lone pairs in N₂X₂. It should be greater in the cis geometry than in the trans, and the *difference* between the repulsions in the cis and trans forms should decrease as the electronegativity of X increases and the lone pairs became more s-like losing their directionality. Thus in N₂H₂ the electrostatic repulsion would dominate favoring the trans isomer whereas in N₂F₂ the hyperconjugative effect prevails making the cis of lower energy.

Mechanism of Cis-Trans Isomerization. There have been two pathways considered for the isomerization process: rotation and inversion (Scheme I). We have investigated Scheme I



the alternatives for the set of substituents, H, F, Me, CN, NH₂, NO₂, and CHO. For all cases investigated, the inversion mechanism, 1 → 3 → 2, was of lower energy. Even small deviations from a planar transition state were found to be of higher energy. The sole exception was HNNNO₂ where a deviation of about 10° from planarity was calculated. Figure 2 shows the potential surface for the N₂H₂ isomerization. The NNH angle is demarcated along the radial lines while the HNNH dihedral angle is varied circumferentially. The low energy path lies along the diameter connecting the cis and trans isomers. The higher energy rotational path involves sweeping out a curved line over the

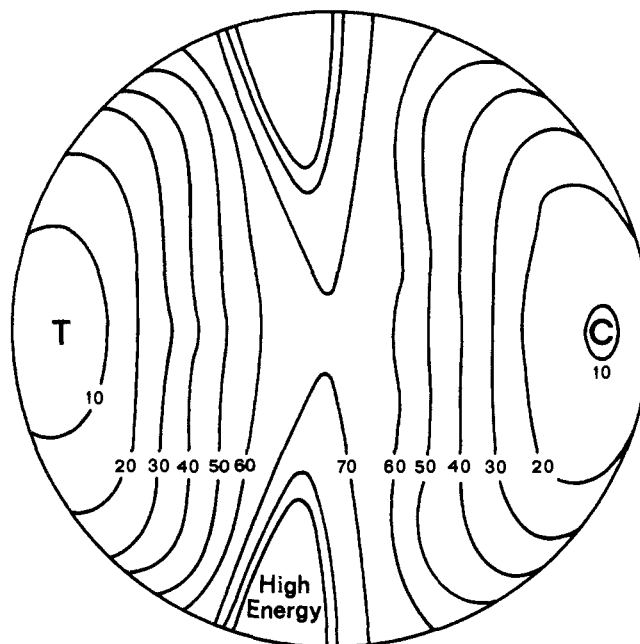


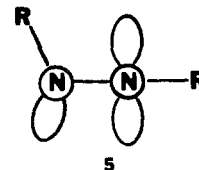
Figure 2. A two-dimensional STO-3G potential surface for the cis-trans isomerization of N₂H₂. The N-N-H angle for the hydrogen undergoing motion is demarcated radially and the H-N-N-H angle circumferentially. C and T refer to the equilibrium geometries of the cis and trans isomers. Energies are given in kcal/mol relative to the trans isomer.

tential surface. Inasmuch as the pure rotation isomerization of N₂H₂ is symmetry forbidden,^{23,37,39} it might be thought that a configuration interaction treatment would be necessary to accurately compare the inversion and rotation pathways. However, Winter and Pitzer³⁹ have recently shown that a multiconfiguration self-consistent field treatment lowers the rotational transition-state energy by only 6.5 kcal/mol, relative to the Hartree-Fock treatment.

It is interesting to compare the energy required to reach the inversion transition state where the NNR' angle is 180°. The following ordering was obtained (with the energies given in kcal/mol relative to the trans isomer) for the diazenes with R = R'

$$F (83.7) > H (66.4) > CH_3 (61.6) > CN (45.6) \quad (2)$$

This ordering is easily rationalized in terms of the π -like interactions that occur in the transition state. At the inversion transition state, the lone pair on the inverting nitrogen has been transformed into a nearly pure p orbital. It will naturally be of high energy and is an excellent π -electron donor into low lying, vacant π^* orbitals of the R' substituent (see structure 5).



Fluorine, a π donor itself, thus has a higher activation energy than the purely σ -bonding hydrogen. The methyl group is capable of some hyperconjugation⁸⁵⁻⁹⁷ with the lone pair but is not as good a π acceptor as the cyano group with its low lying, vacant π^* orbitals. The geometric changes that occur in some of the molecules at the transition state are discussed below.

There exists the intriguing opportunity to investigate, at least theoretically, the possibility of competing modes of isomerization. Given a diazene with two unlike substituents

Table III. Energy of Different Inversion Transition States (kcal/mol) Relative to the Trans Isomer^a

R	R'			
	F	H	CH ₃	CN
F	83.7	53.6	49.5	39.6
H	101.7	66.4	62.4	46.9
CH ₃	101.0	65.8	61.7	47.4
CN	96.2	61.4	57.2	45.6

^aThe NNR' angle is assumed to be 180° at the transition state. Geometries were optimized in the STO-3G calculations. R is the noninverting substituent and R' the inverting substituent.

R and R', we ask which will undergo the inversion. We have carried out calculations considering the two possible transition states for each pairing of substituents from the set F, H, Me, CN. In each case it was, not surprisingly, the better π acceptor which underwent the inversion in the lower energy transition state. Again, it was found that, at least for excursions of up to 30° from linearity, the inversion mechanism was of lower energy than the rotational. Our results are summarized in Table III.

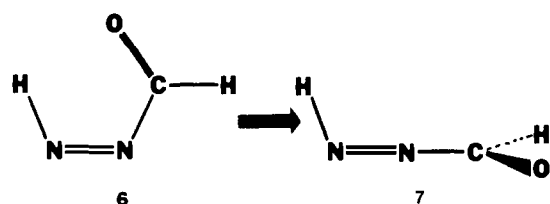
If R, the noninverting group, is held constant and R' is varied, the energy of the transition state ($E(R, R')$) varies in the same overall fashion as for the R = R' series (eq 2).

On the other hand, suppose R', the inverting substituent, is held constant and R varied. For a given choice of R, we find that, when R is H or CH₃, the transition-state energy is higher than when R is F or CN. This follows simply from the total charges on the nitrogens within the diazene group. In the transition state, the inverting nitrogen changes its hybridization to sp thus becoming more electronegative and acquiring a sizable negative charge as shown in Table I. If the R substituent is such that a negative charge resides on the adjacent, noninverting nitrogen, there may be substantial repulsion and a higher activation energy than would otherwise be the case. Examining Table I, a noninverting H or CH₃ allows buildup of charge on N1. Conversely, if the noninverting substituent R is such as to remove charge—either inductively as with F or with the aid of vacant π accepting orbitals as for CN—there should be (and in our calculations is) a noticeable stabilization of the transition state.

The highest occupied molecular orbital is dominated by the lone pair p character of the inverting nitrogen. For a given inverting group, R' (columns in Table III), the HOMO is about 35 kcal/mol higher when R is H or CH₃ than when R is F or CN. The low activation energy of imino carbonates which have electronegative noninverting CH₃O groups has been interpreted⁴⁵ as indicating a polar transition state in which unsharing of the electrons participating in the double bond has taken place facilitating a rotational motion. These arguments might suggest that FNNH, with H inverting, should have a reduced preference for inversion relative to HNNH. However, our calculations show nearly exactly the same preference for the inversion pathway.

Given the importance of the lone-pair-substituent donation in determining the energetics of the isomerization, it was clear that the possibility existed for an inversion mechanism which involved not only an inverting of the N-N-R' bond but also a rotation about the NR' bond axis as the transition state is approached. Both the -NO₂ and -CHO substituents have low lying vacant π^* orbitals and may function as π acceptors. Furthermore, they are single vector systems in that their single π system lies perpendicular to the plane of the substituent atoms. Of course, both -CN and -F possess two orthogonal π systems and we thus term them double vector.

We calculated the energies of the cis and trans isomers for R' being NO₂ or CHO and found the energies to be lower when the π system of the substituent was in conjugation with the diazene double bond than when they were perpendicular to each other. We then calculated the various possible inversion transition states. In both cases a rotation, such as 6 to 7, was involved around the N-NO₂ or N-CHO



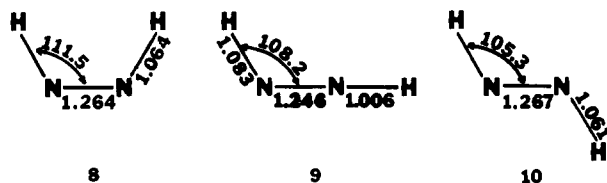
bonds so that the π vector of the substituent was aligned with the lone pair p orbital of the inverting nitrogen. The energy difference between the perpendicular transition state 7 and the corresponding planar ones was significant. For inversion with -NO₂, it was 14.2 kcal/mol, and for -CHO it was 17.2 kcal/mol relative to the better of the two possible planar transition states. For comparison purposes, the possible orientations for the transition states of a singly vectored π donor, NH₂, were also explored. As expected, the reverse situation obtained. The lowest energy transition state was calculated to be with the π vector of the substituent in conjugation with the double bond of the diazene and perpendicular to the p-orbital lone pair of the inverting nitrogen. The geometry changes, detailed below, that occurred in the transition state provide further insight into the interpretation outlined above. Experimental studies on the methylenimine system⁴⁹ have suggested the presence of a rotation of the inverting group as the transition state is approached for single vector π acceptor.

Recently Levin⁸⁴ has elegantly discussed the effect of electronegativity on AH₃ molecule inversion barriers. Although allowing that π effects probably outweigh electronegativity effects, he finds that electronegative substituents lower the inversion barrier. As alluded to above, increasing the electronegativity of the substituents should stabilize the lone pair of the central atom, in pyramidal geometries, by increasing its s character. Thus it will cost more energy to reach the inversion transition state where the lone pair is a pure p orbital.

The HN=N-NH₂ system provides a model system where we may attenuate the repulsive π interaction through rotation about the N-N bond. If the amino lone pair is restricted to the heavy-atom plane, the inversion motion costs either 82.6 or 86.1 kcal/mol depending on orientation of the lone pair to reach the transition state from the trans geometry.

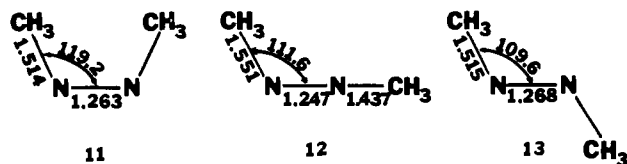
On the other hand, if the amino lone pair is allowed to assume its optimum orientation, approximately perpendicular to the heavy atom plane, the cost of reaching the transition state is reduced to 74.7 kcal/mol. As Table III shows, this is only some 8.3 kcal/mol larger than the corresponding figure for H-N=N-H. In a rough way these data suggest that the π -like repulsion is probably more important than electronegativity effects for the amino substituent.

H-NN-H. A potential surface for the cis-trans isomerization of N₂H₂ is provided in Figure 2. The optimized geometries for cis, inversion transition state, and trans forms are shown in 8, 9, and 10. The corresponding relative energies are 7.4, 66.5 and 0.0 kcal/mol. The shortening of the N=N and inverting N-H bond at the transition state, 9, is easily attributed to the formal change in the hybridization from sp² to sp of the inverting nitrogen. The same trend is observed in extended basis set calculations.⁹⁸ The changes



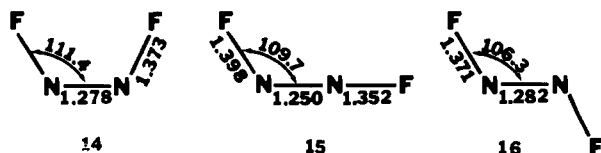
in the optimized geometries are also reflected in the Mulliken population analysis contained in Table I. The N1=N2 overlap population is greater in the cis form than the trans while the N—H overlap population is lower for cis corresponding to the changes in the optimized bond lengths. At the transition state, the N—H overlap population in the bond undergoing inversion is 0.712 (of which 0.342 is due to N(2s)—H(1s) overlap) compared with 0.587 (0.015) for the cis and 0.595 (0.022) for the trans. The hydrogen attached to the inverting nitrogen has become substantially more positive (0.279) probably because of the higher electron attracting ability of the (formal) nitrogen sp hybrid used in the bond.⁹⁹ The dipole moment is 2.4 in the transition state relative to 2.9 in the cis form. (That of the trans form is, of course, zero.)

CH₃—NN—CH₃. We expect that the methyl group will behave nearly the same as the hydrogen substituent. There should, however, be minor perturbations due to the relative electronegativities and the hyperconjugating ability of the methyl group.⁸⁶⁻⁹⁷ The optimized geometries (subject to the constraint that C—H = 1.09 Å and ∠HCH = 109.47°) are shown in structures 11, 12, and 13 and have relative



energies of 6.81, 61.73, and 0.0 kcal/mol. Experimental data¹⁰⁰ (probably for the trans isomer) provides a N=N bond length of 1.24 ± 0.05 Å, and an N—N—C angle of 110 ± 10°. Again the bonds to the inverting nitrogen undergo shortening at the transition state and we attribute the effect to a change in hybridization at the inverting nitrogen. We may inquire to the extent of hyperconjugation by comparing overlap populations of the inverting methyl group carbon p orbitals and hydrogen 1s orbitals to those in either the cis or trans isomers. The average for all three hydrogens is 0.537 for the transition state compared with 0.548 for the cis and 0.550 for the trans. The calculated dipole for the transition state is 2.6 relative to 3.1 for the cis isomer.

F—N=N—F. The fluorine atoms are π donors and σ acceptors. Consequently, we expect the nitrogen π-charge density to be greater in either the cis or trans isomer than was the case for N₂H₂. For the cis isomer, the p_π occupation¹⁰¹ is 1.058 and for the trans 1.055, whereas for N₂H₂ symmetry requires a value of 1.000. The optimized geometries are shown in 14–16 and have relative energies of -0.1,

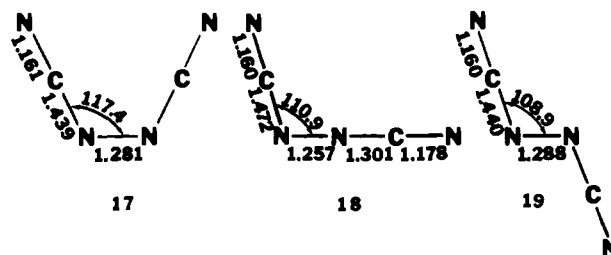


83.7, and 0.0 kcal/mol.¹⁰² These optimized geometries may be compared with the microwave structural determinations for the cis isomer¹⁰³ of N=N being 1.214 ± 0.005 Å, N—F being 1.384 ± 0.01, and ∠NNF being 114.5 ± 0.5°. The N—F undergoing inversion in the transition state has not undergone shortening, relative to either the cis or trans iso-

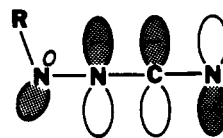
mers to the extent that either N—H or N—Me bonds did. Presumably, this is due to the net antibonding interaction between the fluorine lone pair and the p-type lone pair of the nitrogen undergoing inversion. The 2p_xN—2p_xF (in the plane of the transition state) overlap population at the inverting center is -0.3757 while the 2p_yN—2p_yF (π system, perpendicular to the nuclear plane) is 0.2487.

The dipole moment of the transition state, 15, was 1.7 as compared with 0.9 for the cis isomer, 14. The isomerization activation energy has been experimentally estimated at 32 kcal/mol.^{65b}

NC—NN—CN. This molecule has been tentatively observed by Marsh and Hermes¹⁰⁴ and ab initio calculations have been performed¹⁰⁵ favoring the trans isomer by 20 kcal/mol. The —CN groups each possess two low lying π* orbitals which may accept π-electron density from the N=N system and the lone pair functions. The geometry optimized molecules are shown in 17–19, which have rela-



tive energies of 6.6, 45.6, and 0.0 kcal/mol. Several results of the donation of charge into the CN π* orbitals, 20, at the



20

transition state may be discerned. First is the lengthening of the CN bond length within the inverting CN group by about 0.018 Å relative to either the cis or trans optimized structures. The bond weakening is also obvious in the overlap populations reported in Table I where there is a pronounced drop in the C—N overlap population for the inverting group. There is an increase in the number of electrons associated with the inverting nitrogen at the transition-state geometry as indicated by the data of Table I. For most molecules it is an increase of about 0.11 electron. However, when —CN is the part of the inverting center, the increase in negative charge is only about 0.08 electron. Presumably, this is attributable to the back donation into the CN π* orbitals. The shortening of the inverting N—C bond is about 0.139 Å, substantially greater than that for an inverting hydrogen or methyl group.

R ≠ R'. Most of the geometric effects described for the R = R' cases above are also discernible when R ≠ R'. The optimized NNR or NNR' bond angles are smaller in the trans isomer than in the cis. The importance of electron accepting in the inverting R' substituent is demonstrable, for instance, in the changes in the inverting CN bond length of the R' = CN group. On the average, it increases by 0.016 Å in going from the trans isomer to the transition state where R' = CN.

There are a number of effects which arise from the interaction of the two substituents. One such effect has been discussed above for calculations on the cis—trans activation energy. Another related effect is shown in Table IV which displays the optimized N=N bond length in the trans isomer as a function of R and R' substituents. Examining the diag-

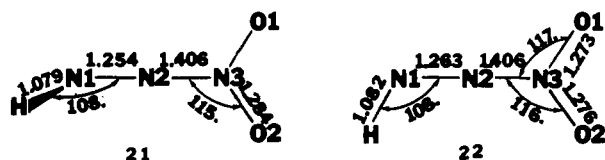
Table IV. Optimized N=N Bond Lengths for the Trans Isomer of the Indicated RN₂R' Molecules

	Trans N=N bond length			
	F	H	CH ₃	CN
F	1.282	1.270	1.270	1.284
H	1.270	1.267	1.268	1.279
CH ₃	1.270	1.268	1.268	1.279
CN	1.284	1.279	1.279	1.288

onal it is seen that the changes roughly parallel the Mulliken overlap populations reported in Table I. The F and CN substituents which function as electron withdrawers, relative to H or CH₃, increases the N=N bond length and decrease the corresponding Mulliken overlap population. The off-diagonal cases where R ≠ R' show situations intermediate between the RN₂R and R'N₂R' molecules.

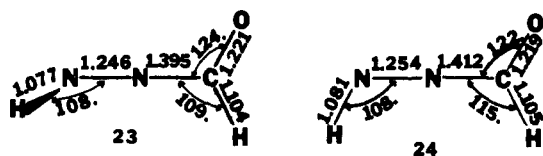
R' = NO₂, CHO, NH₂. These substituents attached to the inverting nitrogen are single vector π systems. We may again examine the importance of interaction in the transition state through the optimized bond lengths of the various inversion transition states.

Structures **21** and **22** are related by a 90° rotation about the N₂N₃ bond. **21**, which is about 14 kcal/mol lower in energy than **22**, has a shorter optimized N2-N3 bond length



and longer N-O distances than **22**, agreeable with the concept of donation into the vacant π* orbital of the NO₂ group.

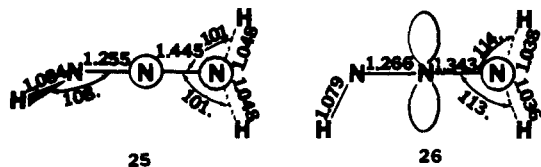
The same phenomenon is observed when R' is -CHO. The low energy inversion transition state is **23** with the carbonyl π* orbital in conjugation with the inverting nitrogens p-type lone pair. **24** is higher in energy by 17.2 kcal/mol and has a longer NC and shorter CO bond lengths.



The C-H σ bond length behaves in the converse fashion, longer in **24** and shorter in **23**.

When R' is NH₂, the favored pure inversion transition state is **25** which minimizes interaction between the adjacent lone pairs. A comparison of the optimized structures provides additional insights.

In **25**, the inverting lone pair is eclipsing the lone pair of the amino group. In order to minimize the repulsive interactions, the amino group has become quite pyramidal relative to **26** where there is conjugation between the double bond



and the NH₂ lone pair. The N-NH₂ bond length in **25** is longer than in **26** partially due to minimizing the repulsive interaction and partially to the rehybridization of the amino nitrogen.

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