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# The Importance of Lone Pair Delocalizations: Theoretical Investigations on the Stability of *cis* and *trans* Isomers in 1,2-Halodiazenes

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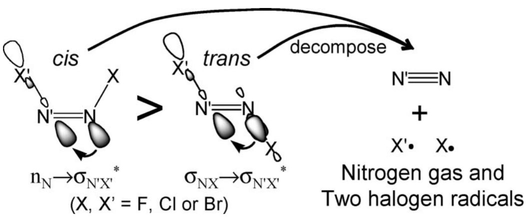

The relative and thermodynamic stabilities of *cis* and *trans* isomers of 1,2-dihalodiazenes (XN=NX; X = F, Cl, or Br) were examined using high level ab initio and density functional theory (DFT) calculations. For 1,2-dihalodiazenes, it was found that the *cis* isomers were more stable than the corresponding *trans* isomers, despite the existence of several *cis* destabilizing mechanisms, such as steric exchange between halogen lone pairs and dipole−dipole electrostatic repulsions ($\Delta_{trans-cis}$ = 3.15, 7.04, and 8.19 kcal mol$^{-1}$, respectively, at BP86/6-311++G(3df,3pd)//B3LYP /6-311++G(3df,3pd) level). Their origin of the *cis*-preferred difference in energy was investigated with natural bond orbital (NBO) analysis to show that the "*cis* effect" came mainly from antiperiplanar interactions (AP effect) between the nitrogen lone pair and the neighboring antibonding orbital of the N−X bond ($n_N \rightarrow \sigma_{N'X'}^*$). The delocalization of halogen lone-pair into the antibonding orbital of the N=N bonds (the LP effects) was also found to enhance the *cis* preference by 1.20 to 6.58 kcal mol$^{-1}$, depending on the substituted halogen atom. The total amount of the AP effect increased as the halogen atom became larger, and the increased AP effect promoted the triple-bond-like nature of the N=N bond (shorter N=N bond length and wider NNX angle). The greater AP effect also made the N′−X′ bond easier to cleave (longer N−X bond length), and a higher energy level than that of the nitrogen lone pair was found in the N−Br bonding orbital in 1,2-dibromodiazenes, thus indicating the significant instability of this molecule. The degradability of the N−Cl bond in 1,2-dichlorodiazenes and the fair stability of the N−F bond in 1,2-fluorodiazenes were also confirmed theoretically, and were found to be consistent with the previous experimental and theoretical reports. These results clearly indicate the dominance of lone-pair-related hyperconjugations on the basic electronic structure and energetic natures of 1,2-dihalodiazene systems.

## 1. Introduction

The nitrogen−nitrogen double bond is popular in textbooks for general organic chemistry. Several diaryl azocompounds are widely used as dyes and pH indicators.[1] Diethyl azodicarboxylate (DEAD) reacts with phosphine to form an important intermediate in the Mitsunobu reaction.[2] Azobisisobutyronitrile (AIBN) is a frequently used radical initiator, which decomposes into nitrogen and two cyanoisopropyl radicals when it is heated or light-irradiated. As such, many molecules possessing an N=N bond are known to be stable under normal conditions and are used for many purposes. Thus, the understanding of their electronic structure as well as the factors determining their geometries has been very important and has been studied for decades. 1,2-Difluorodiazenes (**1**) are known to be the only stable dihalodiazenes. A trace of 1,2-dichlorodiazenes (**2**) seems to have been detected,[3] but nothing has been reported on 1,2-dibromodiazenes (**3**), experimentally and theoretically. Morokuma[4a,c]

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and Schneider[4b] independently calculated the dissociation energy barriers of 1,2-difluorodiazenes (**1**) and 1,2-dichlorodiazenes (**2**) and reached the same conclusion: the former ones (**1**) had large barriers for N—F bond cleavage, while those of N—Cl bond in the 1,2-dichlorodiazenes (**2**) were small, and they instantaneously decompose into nitrogen gas and two chlorine radials. Their discussions on the potential energy surface of **2** were comprehensive and reasonable, but the critical explanation for the chemical weakness of the N—Cl bond was missing.

Because of their availability and simple molecular structures, 1,2-difluorodiazenes (**1**) are well-studied molecules possessing an interesting chemical feature called the "*cis* effect," which has been known for 40 years.[5,6] The *cis* effect of **1** is a physicochemical phenomenon in which its *cis* isomer was experimentally reported to be more stable than the corresponding *trans* isomer by 3.050 ± 0.400 kcal $mol^{-1}$.[6] Furthermore, even though no experimental results have been reported, previous calculations showed that the 1,2-dichlorodiazenes (**2**) also have the *cis* preferable energetic gap between the two isomers (6.8 kcal $mol^{-1}$).[7] Since the *cis* isomers of 1,2-dihalodiazenes are electronically more condensed and have greater dipole—dipole repulsion between the two N—X bonds, this phenomenon is obviously at odds with the valence-shell electron-pair repulsion (VSEPR) theory and hence the origin of this mysterious *cis* effect has been a long-standing question in the field of basic chemistry.[6,8] Wolfe insisted that the sum of the repulsive forces among two nitrogen lone pairs and two N—F bonds was greater in the *trans* isomer, which led the *cis* isomer to be more stable.[9] Epiotis performed the Hartree—Fock (HF) level calculations with 4-31G basis set and qualitatively ascribed the *cis* effect to two delocalization mechanisms: the nitrogen lone-pair delocalization into the antibonding orbital of the neighboring N—F bond, ($n_N \rightarrow \sigma_{N'F'}{}^*$; AP effect) and the out-of-plane lone-pair delocalization of F ($n_{F\pi}$) into the antibonding $\pi$ orbital of the N═N bond ($n_{F\pi} \rightarrow \pi_{NN'}{}^*$; $\pi$-LP effect). However, the contributions of these delocalization mechanisms were not evaluated quantitatively.[10] Skancke indicated that $\pi$ delocalizations including $n_{F\pi} \rightarrow \pi_{NN}{}^*$ were the origin.[11] Recently, Anders performed high-level post-SCF calculations (MP2, B3LYP, and BP86) with 6-311++G(3df,3pd) basis set and concluded that the *cis*—*trans* energy difference came from the lone pair—lone pair repulsion, antiperiplanar interactions, and Coulombic repulsion or attraction between diazene substituents.[7] As such, a number of theories and calculations have been independently or qualitatively performed to explain this phenomenon, but the origin of the *cis* effect in 1,2-dihalodiazenes is still controversial.

Here, high-level ab initio and density functional theory (DFT) calculations have been combined with natural bond orbital (NBO) analysis[12] and orbital phase theory[13] to quantitatively investigate this puzzling *cis*—*trans* energy gap in 1,2-dihalodiazenes (XN═NX; X = **1**, F; **2**, Cl; or **3**, Br), just as we have shown in the *cis* effect on 1,2-dihaloethenes,[14] where the dominant factor was halogen lone pair delocalized into the antibonding orbitals of the C═C bond (LP effect). The unsubstituted 1,2-diazenes (HN═NH: **4**) were used as reference compounds because previous infrared and near-ultraviolet absorption spectrum showed that the *trans* isomer of **4** was the most stable isomer[15] and several theoretical calculations proved the *trans* preference energy difference.[7,16] Moreover, the electronic structures of 1,2-dihalodiazenes were extensively examined from the viewpoint of orbital—orbital interactions to clarify the reason for the particular instability of 1,2-dibromodiazenes (**3**) compared to the reported degradability of 1,2-dichlorodiazenes (**2**), and the fair stability of 1,2-difluorodiazenes (**1**). For further understanding of the electronic structures of 1,2-dihalodiazenes **1—3,** their calculated trends in the geometries and orbital—orbital interactions were compared to the previously reported ones of the 1,2-dihaloethenes which were the electronic isosteres to the 1,2-dihalodiazenes.[14]

## 2. Theoretical Background

**Computational Methods.** All ab initio and DFT calculations including NBO analysis[12] were performed with Gaussian 03 program packages.[17] Pre-NBO orbitals were plotted using Orbplot 2.0.[18] The geometries for the calculations were edited using the vi text editor or Spartan program package.[19] These initial structures

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were optimized at HF, MP2, B3LYP, and B3PW91 levels using a very large 6-311++G(3df,3pd) basis set with 6D option. Then, single-point energies were calculated on B3LYP-optimized structures to accurately evaluate the influence of the electron correlations on *cis*−*trans* energy differences. Furthermore, we performed NBO second-order perturbation analysis[12] at the BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level to quantitatively determine the contributions of two-electron−two-orbital interactions. Natural population analysis (NPA) was also performed at the same level to confirm the mechanism of the *cis* effect from the viewpoint of the electron population.[12a,b] Frequency calculations were performed on all the optimized geometries to avoid imaginary frequencies in all the 1,2-disubstituted and unsubstituted diazenes **1**−**4**.

The NBO second-order perturbation energy ($E_2$), which is often applied to organic molecules,[14,20] is expressed by the following formula,

$$E_2 = q_i \frac{F_{ij}}{\varepsilon_j - \varepsilon_i}$$

where $q_i$ is the electron population of the *i*th donor orbital, $\epsilon_i$ and $\epsilon_j$ are the energy levels of the *i*th and *j*th orbital, and $F_{ij}$ is the (*i*, *j*) element of the Fock matrix.

**Orbital Phase Theory.** The orbital phase continuity−discontinuity theory has been shown to underlie the stabilities of various chemical systems through the delocalization process.[12] According to the principles, the orbital phase of cyclic orbital interactions is an important factor in promoting orbital−orbital interactions. The requirement for orbital phase continuity to stabilize the molecule through the effective delocalization process is as follows: (a) the electron-donating orbitals (denoted by D-D) should be out of phase; (b) the accepting orbitals (denoted by A-A) should be in phase; and (c) the donating and accepting orbitals (D-A) should be in phase.

*trans*-1,2-Dihalodiazene has through-bond $\pi$-orbital interaction in which two halogen $\pi$ lone pairs (p and q) interact with $\pi$-bonding and antibonding orbitals of the N=N bond ($\pi$ and $\pi^*$) (Figure 1). As can be seen in Figure 1a, the orbitals p, q, and $\pi$ are occupied by two electrons in the ground-state G. The process of delocalization from the halogen $\pi$ lone pair into the $\pi$ antibonding orbital of the N=N bond ($n_{X\pi}\rightarrow\pi_{NN}^*$), in which one electron of p or q moves into the vacant $\pi^*$ orbital, is denoted as p−$\pi^*$ or q−$\pi^*$ interaction ($T_1$ or $T_2$). From the point of view of orbital interactions, delocalizations are achieved via the mixing process of G with the $T_1$ or $T_2$ state. Moreover, the locally excited state (E) is formed when one electron in the $\pi$ orbital subsequently shifts into a singly occupied p or q orbital of $T_1$ or $T_2$, which are denoted as $\pi$−p or $\pi$−q interactions. Consequently, we could say that the cyclic -G-$T_1$-E-$T_2$- configuration (or -$\pi$-p-$\pi^*$-q- interaction) occurs in the *trans*-1,2-dihalodiazenes. In this configuration, halogen lone pairs (p and q) and the $\pi$-bonding orbital of N=N ($\pi$) are clearly electron-donating orbitals (denoted as D) and only the $\pi$-antibonding orbital of N=N ($\pi^*$) is an acceptor orbital (denoted as A). Hence, stabilization via through-bond electron delocalization is more effective when the orbital phases of these donors and acceptors are continuous, but as depicted in Figure 1b, the orbital continuity is not satisfied in this through-bond system of *trans*-1,2-dihalodiazenes.

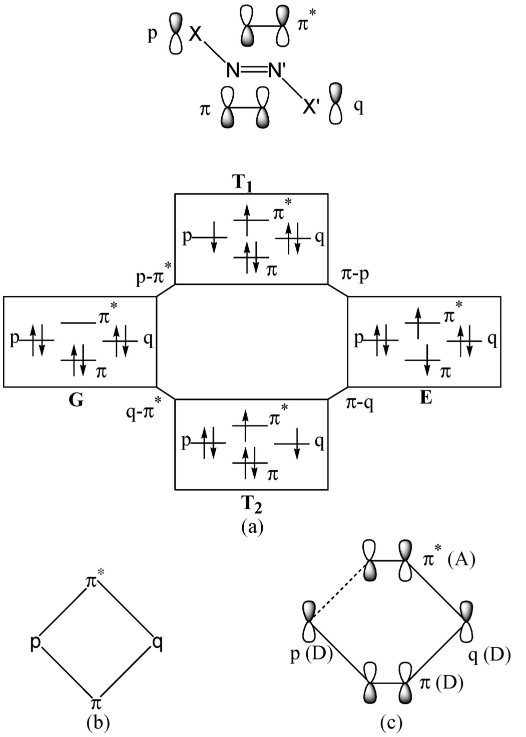

**FIGURE 1.** Through-bond interactions in the $\pi$-LP effect of *trans*-1,2-dihalodiazenes: (a) mechanism of electron delocalizations; (b) cyclic orbital interaction; (c) orbital phase discontinuity.

However, the mechanism in *cis*-1,2-dihalodiazene systems is different because the consideration of through-space interactions between two halogen lone pairs is required. This *cis*-specific interaction could be denoted as p−q interaction in Figure 2a, in which one electron of a doubly occupied p/q orbital moves into a singly occupied q/p orbital. The existence of this interaction changes the mechanism of the electron delocalization system and the triangle interaction, -G-$T_1$-$T_2$- (-$\pi^*$-p-q-), is newly provided (Figure 2b). According to Figure 2c, the -G-$T_1$-$T_2$- configuration is clearly continuous. Because of this speculation, halogen $\pi$ lone-pair delocalization into the $\pi$-antibonding orbital of the N=N bond ($\pi$-LP effect: $n_{X\pi}\rightarrow\pi_{NN}^*$) in *cis*-1,2-dihalodiazenes could be predicted to be greater than in *trans* isomers. In this model, the smaller energy gap between the halogen $\pi$ lone-pair and the $\pi$-antibonding orbital of N=N bond (denoted as $\Delta E$ in Figure 2d) strengthens the -G-$T_1$-$T_2$- (-$\pi^*$-p-q-)-type triangle interaction, while the larger $\Delta E$ weakens the corresponding triangle interaction.[12] Similar models could be provided for the $\sigma$-LP effect system of 1,2-dihalodiazenes as well as their heavier phosphor or arsenic analogous.[21]

## 3. Results and Discussion

**Geometry Optimization.** It has been reported that a high-level theoretical method with sufficient electron correlation should be conducted to reproduce the experimental geometries of 1,2-difluorodiazenes (**1**).[7,22,23] In fact, optimized structures of **1** at the HF level gave far shorter N−F (1.323 and 1.324 Å for *cis* and *trans* isomers, respectively) and N=N bonds (1.189 and 1.186 Å, respectively) than the experimental parameters (N−F bonds: 1.384 or 1.409 Å for *cis* isomer, 1.398 Å for *trans* isomer; N=N bonds: 1.214 or 1.209 Å for *cis* isomer, 1.224 Å for *trans* isomer) (Table 1). On the other hand, the remaining three geometries based on the post-SCF methods, MP2, B3LYP, and B3PW91, were clearly closer to the experiment and proved

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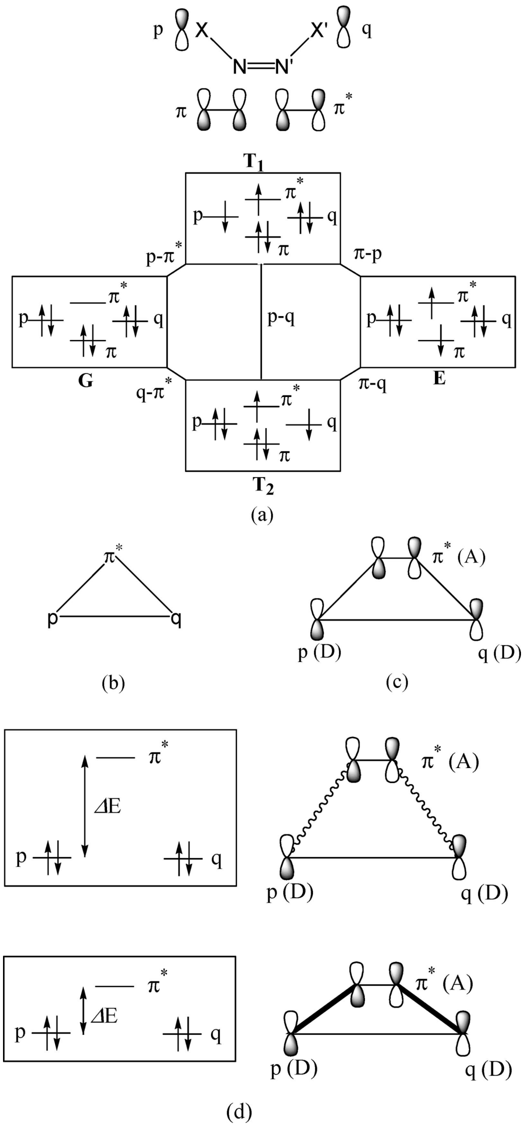

**FIGURE 2.** Through-space interactions in the $\pi$-LP effect of *cis*-1,2-dihalodiazenes: (a) mechanism of electron delocalizations; (b) cyclic orbital interaction; (c) orbital phase properties. (d) The energy gap ($\Delta E$) between halogen $\pi$ lone pair (p and q) and antibonding orbital of N=N bond ($\pi$*) changes the strength of triangle orbital interaction -p-$\pi$*-q-. The large energy gap leads to the weakened orbital interaction (top; denoted as wavy line), while the small energy gap results in the strengthened orbital interaction (bottom; denoted as bold line).

**TABLE 1. Calculated Bond Length and Angles of 1,2-Substituted and Unsubstituted Diazenes, XN=NX (X = F, Cl, Br, or H)[a]**

| | | *cis* | | | *trans* | | |
|---|---|---|---|---|---|---|---|
| X | method | N=N | N−X | N−N−X | N=N | N−X | N−N−X |
| **1**(F) | HF[b] | 1.189 | 1.323 | 114.6 | 1.186 | 1.324 | 107.5 |
| | MP2[b] | 1.229 | 1.375 | 114.2 | 1.238 | 1.373 | 104.9 |
| | B3LYP[b] | 1.209 | 1.387 | 115.1 | 1.216 | 1.381 | 105.8 |
| | B3PW91[b] | 1.209 | 1.373 | 115.1 | 1.216 | 1.368 | 105.9 |
| | BP86[c] | 1.218 | 1.402 | 115.8 | 1.232 | 1.402 | 104.9 |
| | exptl[d] | 1.214(5) | 1.384(10) | 114.5(5) | | | |
| | exptl[e] | 1.209 | 1.409 | 114.4 | 1.224 | 1.398 | 105.5 |
| **2**(Cl) | HF[b] | 1.184 | 1.719 | 122.0 | 1.186 | 1.716 | 111.2 |
| | MP2[b] | 1.221 | 1.755 | 121.2 | 1.241 | 1.740 | 108.5 |
| | B3LYP[b] | 1.191 | 1.795 | 122.6 | 1.206 | 1.782 | 109.5 |
| | B3PW91[b] | 1.196 | 1.764 | 122.2 | 1.211 | 1.753 | 109.5 |
| **3**(Br) | HF[b] | 1.169 | 1.913 | 124.0 | 1.175 | 1.906 | 111.3 |
| | MP2[b] | 1.194 | 1.980 | 123.9 | 1.222 | 1.946 | 108.4 |
| | B3LYP[b] | 1.167 | 2.022 | 125.3 | 1.179 | 2.017 | 109.6 |
| | B3PW91[b] | 1.174 | 1.977 | 124.7 | 1.188 | 1.973 | 109.6 |
| **4** (H) | HF[b] | 1.210 | 1.015 | 112.9 | 1.208 | 1.012 | 108.1 |
| | MP2[b] | 1.254 | 1.035 | 111.6 | 1.255 | 1.030 | 105.8 |
| | B3LYP[b] | 1.235 | 1.039 | 112.9 | 1.236 | 1.033 | 107.0 |
| | B3PW91[b] | 1.232 | 1.038 | 112.8 | 1.233 | 1.033 | 106.9 |
| | exptl[f] | | | | 1.252(2) | 1.028(5) | 106.51(28) |

[a] Structural data are given in angstroms and degrees. [b] 6-311++G(3df,3pd) basis set was used. [c] 6-311++G(3df,3pd) basis set was used, ref 7. [d] Microwave spectroscopy data, ref 24. [e] Electron diffraction data, ref 25. [f] Infrared absorption spectra data, ref 26.

the strong influence of electron correlation on both the N−F and N=N bonds. Among these structures, MP2-optimized ones had rather longer N=N bonds (1.229 and 1.238 Å for *cis* and *trans* isomers, respectively) and shorter N−F bonds (1.375 and 1.373 Å, respectively) compared to the experimental results, presumably because of the overestimation of electron correlation. The applied DFT methods, B3LYP and B3PW91, showed good agreement with the experimental geometries, but we chose B3LYP structures for further single-point energy calculations, since the reliability of this method has already been reported for 1,2-dihalodiazene systems (**1**).[23] The structure optimizations were also conducted at the same level for 1,2-dichlorodiazenes (**2**), 1,2-dibromodiazenes (**3**), and the reference compounds 1,2-diazenes (**4**) (Table 1).

For the obtained B3LYP optimized structures, N=N bond length of *cis*-1,2-diflurodiazenes (1.209 Å) is shorter than that of the corresponding *trans* isomer (1.216 Å), both of which showed good agreement with the experiments (1.214 or 1.209 Å for *cis* isomer, 1.224 Å for *trans* isomer, respectively) (Table 1). On the other hand, N−F bond length in the *cis* isomer (1.387 Å) is longer than its *trans* counterpart (1.381 Å) (experimental values: 1.384 or 1.409 Å for *cis* isomer, 1.398 Å for *trans* isomer). These structural trends were clearly opposite to the 1,2-dihaloethenes where C=C bonds in the *cis* isomers and C−X bonds in the *trans* isomers were longer than those in the other isomers.[14] Changes in their structural parameters might imply differences in their electronic states. The NNF angles in the *cis* isomer like those in 1,2-dihaloethenes are greater and indicate the existence of repulsive forces (N−F dipole moment repulsions and lone pair/lone pair repulsions) or hyperconjugation mechanisms possessing structural influences on the molecules.[14] These trends were also found in both the 1,2-dichlorodiazenes (**2**) and the 1,2-dibromodiazenes (**3**) with the N=N bonds being shorter going down the periodic table: N=N bond lengths are 1.209, 1.191, and 1.165 Å in *cis*-**1**, *cis*-**2**, and *cis*-**3**, respectively. The same trend was found for their *trans* isomers (Table 1). Moreover, it should be noted that the molecules possessing larger halogen atoms have wider NNX angles: 115.1, 122.6, and 125.3° in *cis*-**1**, *cis*-**2**, and *cis*-**3**, respectively. Their *trans* isomers also showed the same tendency (Table 1).

**Cis−trans Energy Differences.** Subsequent single-point energy calculations were performed on the B3LYP/6−311++G(3df,3pd) geometries using a variety of methods (Table 2). In the 1,2-difluorodiazenes (**1**), the HF calculations showed poor results compared to the experimental value (3.05 kcal mol$^{-1}$ *cis* preference; Table 2), even with the very large 6−311++G(3df,3pd) basis set. This result indicated that the electron correlation has a strong influence on the *cis*−*trans* energy difference. As Jursic[23] and Anders[7] described, the BP86 method, a nonlocal DFT, reproduced the experimental energy difference almost perfectly. All of the MP2, B3LYP, and B3PW91 level calculations were good, but they were not comparable with the BP86 result. MP4(SDTQ) and QCISD(T),

**TABLE 2. Calculated *cis*−*trans* Energy Differences (Including the ZPE) of 1,2-Substituted and Unsubstituted Diazenes, XN═NX (X = F, Cl, Br, or H) (kcal mol$^{-1}$, the Positive Number Indicates *cis* Preference)**

| method[a] | **1** (F) | **2** (Cl) | **3** (Br) | **4** (H) |
|---|---|---|---|---|
| HF[b] | −1.82 | −3.03 | −3.14 | −6.07 |
| B3LYP[c] | 1.67 | 4.14 | 4.73 | −5.03 |
| B3PW91[d] | 1.64 | 4.16 | 4.77 | −5.08 |
| MP2[e] | 1.30 | 3.75 | 5.36 | −5.42 |
| MP4(SDTQ)[c] | 1.85 | 4.36 | 6.15 | −5.14 |
| QCISD(T)[c] | 1.43 | 3.52 | 4.63 | −5.06 |
| MP4(SDTQ)[e] | 1.71 | 4.20 | 5.78 | −5.18 |
| QCISD(T)[e] | 1.37 | 3.58 | 4.70 | −5.07 |
| BP86[c] | 3.15 | 7.04 | 8.19 | −4.62 |
| exptl[f] | 3.050 ± 0.400 | | | |

[a] All single point energy calculations were performed using 6-311++G(3df,3pd) basis set. [b] HF/6-311++G(3df,3pd) optimized geometries were used. [c] B3LYP/6-311++G(3df,3pd) optimized geometries were used. [d] B3PW91/6-311++G(3df,3pd) optimized geometries were used. [e] MP2/6-311++G(3df, 3pd) optimized geometries were used. [f] Reference 6.

**TABLE 3. NBO 2nd-Order Perturbation Analysis Calculations for 1,2-Substituted or Unsubstituted Diazenes, XN═NX (X = F, Cl, Br, or H) (kcal mol$^{-1}$)[a]**

| | | AP and SP effects[b] | | | LP effect[c] | | | |
|---|---|---|---|---|---|---|---|---|
| X | | $n_N \rightarrow \sigma_{N'X'}*$ | $\sigma_{NX} \rightarrow \sigma_{N'X'}*$ | subtotal[d] | $n_{X\sigma} \rightarrow \sigma_{NN'}*$ | $n_{X\pi} \rightarrow \pi_{NN'}*$ | subtotal[d] | total |
| **1** (F) | *cis* | 15.40 | 2.04 | 34.88 | 4.93 | 16.61 | 43.08 | |
| | *trans* | 2.83 | 6.40 | 18.46 | 3.36 | 14.89 | 36.50 | |
| | Δ[e] | | | 16.42 | | | 6.58 | 23.00 |
| **2** (Cl) | *cis* | 20.83 | 3.60 | 48.86 | 2.10 | 11.54 | 27.28 | |
| | *trans* | 0.46 | 12.70 | 26.32 | 2.44 | 10.03 | 24.94 | |
| | Δ[c] | | | 22.54 | | | 2.34 | 24.88 |
| **3** (Br) | *cis* | 19.46 | 10.79 | 60.50 | 0.66 | 6.67 | 14.66 | |
| | *trans* | 0.13 | 21.45 | 43.16 | 1.46 | 5.27 | 13.46 | |
| | Δ[c] | | | 17.34 | | | 1.20 | 18.54 |
| **4** (H) | *cis* | 7.04 | 1.63 | 17.34 | - | - | - | |
| | *trans* | 1.72 | 6.03 | 15.50 | - | - | - | |
| | Δ[c] | | | 1.84 | - | - | - | 1.84 |

[a] BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd). [b] *anti* periplanar and *syn* periplanar interactions. [c] The delocalization of halogen lone pairs into the antibonding orbitals of the N═N bond. [d] Total value of AP and SP effects or LP effect. The values are doubled because two sets of same interactions exist. [e] The Δ denotes the *cis*−*trans* energy difference in the total value of AP and SP effects or LP effect.

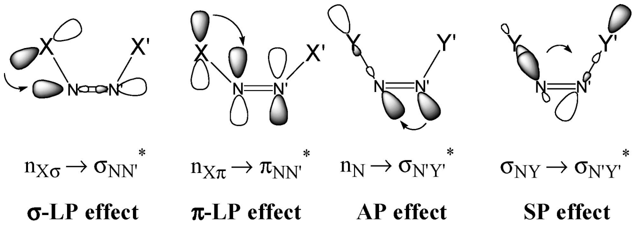

**FIGURE 3.** Definitions of the halogen lone pair ($n_{X\sigma}$ and $n_{X\pi}$) delocalization effects (σ- or π-LP effect), the *anti* periplanar interaction (AP effect), and the *syn* periplanar interaction (SP effect) within the NBO framework for *cis*-XN═N′X′ (X, X′ = F, Cl, or Br) or *cis*-YN═N′Y′ (Y, Y′ = F, Cl, Br, or H).

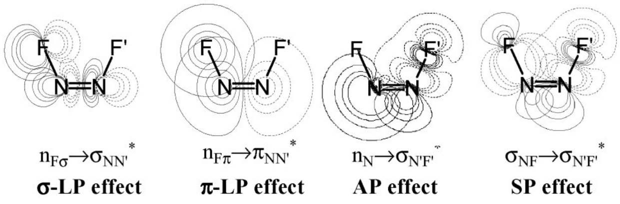

**FIGURE 4.** The fluorine lone pair ($n_{F\sigma}$ and $n_{F\pi}$) delocalization effect (σ- or π-LP effect), the *anti* periplanar interaction (AP effect), and the *syn* periplanar interaction (SP effect) as pre-NBO interactions calculated at the BP86/6-311+G(3df)//B3LYP/6-311+G(3df) level for *cis*-1,2-dihalodiazene. Orbital contours were calculated at the same level for two interacting orbitals in each scheme.

which are extremely high-level ab initio methods, provided a similar energy difference as MP2 and B3LYP calculated methods.

On the basis of the energies calculated at the BP86 level, *cis*-1,2-dichlorodiazene was 7.04 kcal mol$^{-1}$ more stable than the corresponding *trans* isomer, consistent with the electronic energy difference of 6.8 kcal mol$^{-1}$ reported by Anders.[7] Furthermore, 1,2-dibromodiazenes (**3**) show the largest 8.19 kcal mol$^{-1}$ *cis* preference energy difference, implying that the *cis*−*trans* energy gap increased as the size of the substituted halogen atoms increased. The 1,2-diazenes (**4**) showed good agreement with experiments in which the *trans* isomer was the most stable one.[14] The calculated *trans* preference energy difference in **4** was 4.62 kcal mol$^{-1}$ which was close to the previously reported energy difference of 4.9 kcal mol$^{-1}$ based on the high-level theoretical method.[7] These opposing results among 1,2-dihalodiazenes (**1**−**3**) and 1,2-diazenes (**4**) clearly imply that their substituents play key roles in energetic conversion between their *cis* and *trans* isomers.

**NBO Second-Order Perturbation Analysis.** To determine the dominant factors in their *cis*−*trans* energy differences, NBO second-order perturbation analysis was performed at the BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,pd) level (Table 3).

First, the delocalization of halogen lone pairs into the antibonding orbitals of the N═N bond (LP effect) was found to be an important *cis*-stabilizing mechanism for 1,2-dihalodiazenes (**1**−**3**) (Figures 3 and 4), as explained above with the orbital phase theory, that is, the cyclic orbital interaction was continuous only in the *cis* isomers of **1**−**3**. Moreover, the heavier halogen atom provides the smaller orbital−orbital energy gaps for the $n_{X\pi} \rightarrow \pi_{NN'}*$ interactions (π-LP effect) (Table 4), leading to the stronger -G-T$_1$-T$_2$- (-π-p-q-)-type triangle orbital interactions and the larger *cis*-stabilizing energies. However, the overlap of π halogen lone pair ($n_{X\pi}$) and π antibonding orbital of N═N bond ($\pi_{NN'}*$) were decreased because of the longer N−X bond length as the halogen atom got heavier (see the Fock matrix element $F_{ij}$ in Table 4). This decrease in the orbital−orbital overlap gave smaller energetic gain through the π-LP effect. Consequently, the energy differences of π-LP effect were 3.44, 3.02, and 2.80 kcal mol$^{-1}$ *cis* preferable for **1**, **2**, and **3**, respectively. On the other hand, the $n_{X\sigma} \rightarrow \sigma_{NN'}*$ interaction (σ-LP effect) only stabilized the *cis* isomer in 1,2-difluorodiazenes (**1**) by 3.14 kcal mol$^{-1}$, but it worked as a stabilizer for the *trans* isomers relative to the *cis* isomers in 1,2-dichlorodiazenes (**2**) and 1,2-dibromodiazenes (**3**) (their *trans*-stabilizing effects are 0.68 and 1.60 kcal mol$^{-1}$ for **2** and **3**, respectively). These results for the σ-LP effect were clearly at odds with orbital phase theory, but this exception might be ascribable to the difference in N−X bond lengths between the two isomers. The combination of longer N−X bond lengths and condensed halogen σ-lone pairs led to smaller orbital−orbital overlaps in the *cis* isomers compared to those in the *trans* isomers. In fact, the N−X bonds in the *cis* isomers were longer than those in their *trans* forms, especially in the compounds with heavier halogen atoms. Collectively, the total amount of σ- and π-LP effects was *cis* preference by 6.58, 2.34, and 1.20 kcal mol$^{-1}$ for **1**, **2**, and **3**,

**TABLE 4. Fock Matrix Elements ($F_{ij}$) and Orbital−orbital Energy Differences ($\epsilon_i - \epsilon_j$) of AP, SP, and LP Effects in 1,2-Substituted or Unsubstituted Diazenes, XN═NX (X = F, Cl, Br, or H) via NBO 2nd Perturbation Analysis (au)[a]**

| | *cis* | | | | *trans* | | | |
|---|---|---|---|---|---|---|---|---|
| | $n_N \rightarrow \sigma_{N'X'}^*$ | $\sigma_{NX} \rightarrow \sigma_{N'X'}^*$ | $n_{X\sigma} \rightarrow \sigma_{NN'}^*$ | $n_{X\pi} \rightarrow \pi_{NN'}^*$ | $n_N \rightarrow \sigma_{N'X'}^*$ | $\sigma_{NX} \rightarrow \sigma_{N'X'}^*$ | $n_{X\sigma} \rightarrow \sigma_{NN'}^*$ | $n_{X\pi} \rightarrow \pi_{NN'}^*$ |
| | | | | $F_{ij}$ | | | | |
| **1** (F) | 0.081 | 0.038 | 0.059 | 0.061 | 0.036 | 0.066 | 0.047 | 0.058 |
| **2** (Cl) | 0.089 | 0.041 | 0.038 | 0.043 | 0.014 | 0.075 | 0.040 | 0.040 |
| **3** (Br) | 0.085 | 0.058 | 0.023 | 0.032 | 0.007 | 0.080 | 0.033 | 0.028 |
| **4** (H) | 0.063 | 0.034 | *b* | *b* | 0.032 | 0.065 | *b* | *b* |
| | | | | $\epsilon_i - \epsilon_j$ | | | | |
| **1** (F) | 0.53 | 0.86 | 0.96 | 0.27 | 0.55 | 0.85 | 0.91 | 0.27 |
| **2** (Cl) | 0.46 | 0.54 | 0.93 | 0.19 | 0.48 | 0.55 | 0.93 | 0.19 |
| **3** (Br) | 0.44 | 0.36 | 0.98 | 0.18 | 0.44 | 0.37 | 1.04 | 0.18 |
| **4** (H)[a] | 0.71 | 0.86 | *b* | *b* | 0.74 | 0.87 | *b* | *b* |

[a] BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd). [b] No halogen atoms.

**TABLE 5. Natural Population Analysis of 1,2-Substituted or Unsubstituted Diazenes, XN═NX (X = F, Cl, Br, or H)[a]**

| X | atom | *cis* | *trans* | $\Delta$[b] |
|---|---|---|---|---|
| **1** | N | 0.20631 | 0.18856 | 0.01775 |
| (F) | F | −0.20631 | −0.18856 | −0.01775 |
| **2** | N | −0.08340 | −0.13522 | 0.05182 |
| (Cl) | Cl | 0.08340 | 0.13522 | −0.05182 |
| **3** | N | −0.07207 | −0.12570 | 0.05363 |
| (Br) | Br | 0.07207 | 0.12570 | −0.05363 |
| **4** | N | −0.27376 | −0.29482 | 0.02106 |
| (H) | H | 0.27376 | 0.29482 | −0.02106 |

[a] BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level. [b] The Δ denotes differences between *cis* and *trans* isomers.

respectively (Table 3). Clearly, these LP effects play effective roles in the *cis* effect, especially for 1,2-difluorodiazenes (**1**). 1,2-Diazenes (**4**), possessing no halogen lone pairs, could not gain any stabilizing energy via LP effects. This should be an important reason for *trans* preference in this molecule.

Second, the most important hyperconjugation was found to be the $n_N \rightarrow \sigma_{N'X'}^*$ interaction in which two orbitals were located at the advantageous antiperiplanar position only in the *cis*-1,2-dihalodiazenes (AP effect: Figures 3 and 4), due to the larger orbital−orbital overlaps compared to the corresponding syn-periplanar interaction (SP effect) in the *trans* isomers. Another periplanar-type interaction $\sigma_{NX} \rightarrow \sigma_{N'X'}^*$ yielded smaller stabilizing energies in **1** and **2** than those of $n_N \rightarrow \sigma_{N'X'}^*$ interactions, to make their *trans* forms more stable than the corresponding *cis* isomers by 8.72 and 18.2 kcal mol$^{-1}$, respectively. As such, the combinations of $n_N$ and $\sigma_{N'X'}^*$ were the most effective periplanar-type hyperconjugations in **1** and **2**, because of the smallest energy gaps between two interacting orbitals (Table 4). Here, an interesting trend was found in the $\sigma_{NX} \rightarrow \sigma_{N'X'}^*$ interactions: the stabilizing energy through this hyperconjugation increased as the halogen atom increased in size (Table 3). As clearly seen in Table 4, this trend mainly came from both the greater orbital−orbital overlaps (Fock matrix element, $F_{ij}$) and the smaller energy differences between two interacting orbitals ($\epsilon_i - \epsilon_j$) as the substituted halogen atom increases in size. It should be noted that the difference in orbital energy level ($\epsilon_i - \epsilon_j$) in the $\sigma_{NBr} \rightarrow \sigma_{N'Br'}^*$ interaction was smaller than that in $n_N \rightarrow \sigma_{N'Br'}^*$ in 1,2-dibromodiazenes (**3**) (Table 4), indicating that the energy level of bonding orbitals $\sigma_{NBr}$ are higher than that of nitrogen lone pair $n_N$. We could say that this "strange" calculated result might be the theoretical evidence for the nonexistence of 1,2-dibromodiazenes (**3**), because of the instability of N−Br bonds. Thus, even though 1,2-dibromodiazenes (**3**) have no imaginary frequencies at any level of calculation, **3** could be regarded as imaginary molecules. In 1,2-dichlorodiazenes (**2**), the orbital energy level of $n_N$ was calculated to be slightly higher than that of $\sigma_{NCl}$ (0.08 and 0.07 au for *cis* and *trans* isomers, respectively, Table 4), but their differences were far smaller than those for stable 1,2-difluorodiazenes (**1**) (0.33 and 0.30 au, respectively), implying that N−Cl bonds are barely bound and the stabilities of 1,2-dichlorodiazenes (**2**) are very delicate. This observation for **2** is consistent with Morokuma's ab initio calculations.[4a]

Compared to the *anti* periplanar-type interactions (AP effect), all of the corresponding *syn* periplanar interactions (SP effect) were small because of their smaller orbital−orbital overlaps (Tables 3 and 4), and thus they could be classified as secondary periplanar hyperconjugation for the energetic difference between *cis* and *trans* isomers. As such, the AP effect is more important than the SP effect and the total amount of these periplanar interactions is greater in the *cis* isomers for all the 1,2-dihalodiazenes (**1**, 16.42; **2**, 22.54; **3**, 17.34 kcal mol$^{-1}$, respectively; Table 3). The combination of these strong periplanar-type hyperconjugations in the 1,2-dihalodiazene systems obviously promote the triple-bond-like nature of the N═N bond and make the N′−X′ bond easier to cleave. In other words, these periplanar interactions could be considered as an "intramolecular $S_N2$-type reaction" in which the nitrogen lone pair is regarded as a nucleophile to attack the adjacent N′−X′ bond. As a result, strong periplanar interactions could promote the decomposition of 1,2-dihalodiazenes to yield $N_2$ and two halogen radicals,[4] just as an AIBN decomposes into nitrogen gas and two cyanoisopropyl radicals, especially for the ones with larger halogen atoms. In fact, shorter N═N bond lengths and longer N−X bond lengths in all of the *cis* isomers of **1**−**3** could be seen as the structural expression of electronic dominance of these periplanar interactions, especially AP effects, as the primary origin of the *cis* effect in 1,2-dihalodiazene systems (Table 1). Furthermore, the enhanced triple-bond-like nature of the N═N bond should ensure that the nitrogen atom is close to sp hybridization, resulting in wider NNX angles as found in the geometries obtained for **1**−**3**.

However, in the case of 1,2-diazenes (**4**), the *cis*-stabilizing energy difference of AP and SP effects drastically decreased to only 1.84 kcal mol$^{-1}$. This significant difference compared to that in the 1,2-dihalodiazenes (**1**−**3**) could be ascribed to the higher $\sigma_{NH}^*$ orbital energy level than those of $\sigma_{NX}^*$ (X = F, Cl, or Br) because of the higher electro-negativity of the halogen atoms. This difference yielded a larger orbital−orbital energy gap ($\epsilon_i - \epsilon_j$) for both periplanar-type $n_N \rightarrow \sigma_{N'H'}^*$ and $\sigma_{NH} \rightarrow \sigma_{N'H'}^*$ hyperconjugations which led to a smaller amount of stabilizing energy on 1,2-diazenes (**4**) compared to their halogenated derivatives **1**−**3** (Tables 3 and 4). These small periplanar effects as well as the nonexistence of an LP effect in the simple 1,2-diazenes (**4**) were ascribable to the *trans*-preference energy gap between the two isomers.

The additional natural population analysis (NPA) calculations showed apparent existence of N−X dipoles in **1**−**4** (Table 5),

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which repel each other only in the *cis* isomers to produce the *cis*-destabilizing energies. Furthermore, the NPA results supported the dominance of periplanar-type interactions, because all of the nitrogen atoms in the *cis* isomers had more positive charges than those in the corresponding *trans* isomers for all 1,2-dihalodiazenes (**1**−**3**) and 1,2-diazenes (**4**) (Table 5). This tendency implied that the nitrogen atoms in the *cis* isomers were better electron donors than those in the corresponding *trans* isomers for **1**−**4**, owing to the dominant delocalization from the nitrogen lone pair to the antibonding orbital of N−X (X = F, Cl, Br, or H). Interestingly, this trend was completely opposed to the results for 1,2-dihaloethenes in which the LP effect was the major origin of the *cis* effect and the carbon atoms in the *cis* isomers had more negative charges than those in the corresponding *trans* isomers.[14] Furthermore, as mentioned above, the *cis*−*trans* difference in the structural parameters also showed opposite tendencies between the 1,2-dihalodiazenes and the 1,2-dihaloethenes, reflecting the difference in their dominant hyperconjugation mechanisms to determine their geometrical characteristics. Thus, although the 1,2-dihalodiazenes were electronic isosteres to the 1,2-dihaloethenes, the electronic structure and geometrical natures of the two isomers were found to be completely opposite. This reversion seems to be due to the strong electron-donating effect of the nitrogen lone pairs compared to the ordinary covalent bonds (C−H or C−X; X = F, Cl, or Br) in 1,2-dihaloethenes. The longer N−X bond length compared to the C−X bond could also contribute to the difference in the hyperconjugative systems, owing to the production of a smaller LP effect in the 1,2-dihalodiazene systems compared with those in the 1,2-dihaloethenes. As a result, 1,2-dihalodiazenes have a larger AP effect than LP effect, whereas 1,2-dihaloethenes show a greater LP effect than AP effect, but both of these molecules have an apparent *cis* effect through lone-pair hyperconjugation mechanisms which work as counterparts against existing repulsive forces in the *cis* isomers. Moreover, these differences in the electronic structure of 1,2-dihalodiazenes and 1,2-dihaloethenes might have a critical influence on their thermodynamic stability and existence under normal conditions.

## 4. Conclusions

The *cis*−*trans* energy differences in 1,2-dihalodiazenes (halogen = F, Cl, or Br) were investigated using high-level ab initio and DFT calculations and it was found that not only 1,2-difluorodiazenes (**1**) and 1,2-dichlorodiazenes (**2**), but also 1,2-dibromodiazenes (**3**) have the *cis*-preferable energy differences of 3.15, 7.04, and 8.19 kcal mol$^{-1}$, respectively, at the BP86/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) level calculations. According to subsequent NBO second-perturbation analysis, we have shown that the combined *cis* preference energy, namely the periplanar effects (AP and SP effects: 16.42, 22,54, and 17.34 kcal mol$^{-1}$ for **1**, **2**, and **3**, respectively) and the halogen lone pair effects (LP effect: 6.58, 2.34, and 1.20 kcal mol$^{-1}$), stabilize the *cis* isomers by 23.00, 24.88, and 18.54 kcal mol$^{-1}$, respectively, compared with their *trans* counterparts. These large stabilizing energies for the *cis* isomers should override various repulsive destabilization energies, such as Pauli repulsion between the halogen lone pairs and the electrostatic repulsive forces between the N−X (X = F, Cl, or Br) dipoles, to produce the *cis* effect in the 1,2-dihalodiazenes. The fact that the parent diazene (HN=NH) exists exclusively as the *trans* form may suggest that the AP effects ($n_N \rightarrow \sigma_{N'H'}^*$) alone could not cause *cis* preference. In addition, extraordinarily high energy levels of N−Br bonding orbitals in 1,2-dibromodiazenes (**3**) were found to indicate their nonexistence as a result of strong interactions, which decreased the bonding character between nitrogen and bromine atoms, while the N−F bonds in 1,2-difluorodiazenes (**1**) were calculated to be stable and the N−Cl bonds in 1,2-dichlorodiazenes (**2**) were degradable. These observations are in good agreement with previous experimental and theoretical results in which 1,2-difluorodiazenes were found to be stable under normal conditions, 1,2-dichlorodiazenes were barely bound, and 1,2-dibromodiazenes have never been reported to date. These findings, primarily determined through orbital−orbital hyperconjugations, could provide the basic electronic structure of a molecule. Moreover, the importance of lone pair delocalization of heteroatoms must once again be stressed in understanding molecular structures and electronic states in general organic chemistry.[27]

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**Supporting Information Available:** The tables of the absolute energies, relative energy differences, the occupancies of related NBOs, and the three-dimensional coordinates of all optimized structures are provided. The calculated result of natural steric analysis was also shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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