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MO Theoretical Investigation of the Cis Effect Observed in Mono- and Dihalodiazenes

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The relative energies of the different isomers of diazene **2** and its mono and dihalogeno derivatives **1** and **3**−**6** have been calculated using ab initio (up to the MP2/6-311+G*//MP2/6-311+G*), DFT (up the to BP86/6-311++G(3df,3pd)//BP86/6-311++G(3df,3pd level), and semiempirical (MNDO, AM1, and PM3) methods. The aim of this investigation was to determine the magnitude and the electronic origin of the experimentally observed stabilization of the cis isomer relative to the trans form for a series of mono and dihalodiazenes **1** and **3**−**6**. Our calculations revealed that the energetical preference of the cis isomer **1a** is a characteristic property of a wide variety of halogeno-substituted diazenes such as **1** and **3**−**6**. We succeeded in showing that the cis effect is the sum of three different electronic interactions: (a) the lone pair/lone pair repulsion, (b) the negative hyperconjugation, and (c) the Coulombic repulsion or attraction between the diazene substituents. These findings led to the development of a model which allows the interpretation of the relative stabilities of a wide variety of related compounds.

Introduction

There is a lack of quantitative information about the relative stability of compounds containing a nitrogen atom with a coplanar lone pair (lp) on an adjacent atom. This dearth is documented by investigations dealing with the general aspect of tautomerism especially in heterocyclic ring systems containing two adjacent nitrogens and/or further heteroatoms[1,2] A more recent interest in the energetical relationships between the different isomers of substituted diazenes due to the enormous success of the Mitsunobu reaction[3−5] has become increasingly evident. Understanding the first step of this reaction requires information about the relative stability of the cis isomer as compared with the trans form. In addition, the magnitude of the so-called cis effect[6−8] observed for the reactive azenes is of interest. Unfortunately, semiempirical methods are not capable of correctly modeling the cis effect and our first attempts to simulate the phosphorylation step of the Mitsunobu reaction by means of AM1 calculations were not very encouraging.[9]

We report in this paper upon higher level ab initio investigations which finally allowed the quantitative determination of several electronic properties which contribute to the cis effect in the diazene series.[10] To find suitable compounds which permitted calculations at an acceptable level of theory and which are related to the Mitsunobu reagent, we calculated a series of mono- and disubstituted diazenes (Figure 1).

The experimentally found cis effect in difluorodiazene (**1a** as compared to **1b**) has been known for more than 40 years.[11a] Since the first ab initio quantum chemical study of difluorodiazene in 1976,[12] ab initio[12−15] and, more recently, DFT[16,17] calculations have become increasingly important. The structural results and energy differences reported by Jursic[16] (DFT calculations) appear to be very promising. Nevertheless, none of these authors have published convincing explanations for difluorodiazenes preference for the cis isomer. We therefore reinvestigated the difluorodiazene system **1** and then extended our

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[1] (a) Cativiela, C.; Garcia, J. I.; Fayet, J. P.; Elguero, J. *J. Soc. Bull. Chim. Belg.* **1995**, *104* (6), 383. (b) Tomas, F.; Catalan, J.; Perez, P.; Elguero, J. *J. Org. Chem.* **1994**, *59* (10), 2799. (c) Catalan, J.; Sanchez-Cabezulo, M.; De Paz, J. L. G.; Elguero, J.; Taft, R. W.; Anvia, F. *J. Comput. Chem.* **1989**, 462.

[2] Parchment, O. G.; Hillier, I. H.; Green, D. V. S.; Burton, N. A.; Morley, J. O.; Schaefer, H. F., III *J. Chem. Soc., Perkin Trans. 2* **1992**, 1681 and references therein.

[3] Mitsunobu, O. *Synthesis* **1981**, 1.

[4] Mitsunobu, O.; Kato, J. *J. Org. Chem.* **1970**, *45*, 4227.

[5] Hughes, D. L. *Org. React.* **1992**, *42*, 335.

[6] Armstrong, G. T.; Marantz, S. J. *J. Chem. Phys.* **1963**, 169.

[7] Binenboym, J.; Burcat, A.; Lifshitz, A.; Shamir, J. *J. Am. Chem. Soc.* **1966**, *88*, 5039.

[8] Boyle, L. L.; Hudson, R. F.; Wallis, J. D. *J. Mol. Struct. (THEOCHEM)* **1995**, *341*, 141.

[9] Nordhoff, K. Ph.D. Dissertation, University of Jena, Germany, 1998.

[10] For completeness, we refer to a series of investigations on cis-preferred substituted ethylenes: (a) Brockway, L. O. *J. Phys. Chem.* **1937**, *41*, 185. (b) Binkley, J. S.; Pople, J. A. *J. Chem. Phys. Lett.* **1977**, 197. (c) Skancke, A.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4063. (d) Reed, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (e) David, S.; Eisenstein, O.; Hehre, W. J.; Salem, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 3806. (f) For "Sterical attraction" see: Bingham, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 535. Reference 10b.

[11] For fundamental research, compare: (a) Pitzer, K. S.; Hollenberg, J. L. *J. Am. Chem. Soc.* **1954**, *76*, 1494. (b) Bohn, R. K.; Bauer, S. H. *Inorg. Chem.* **1967**, *6*, 309. (c) Kuczkowski, R.; Wilson, D.. *J. Chem. Phys.* **1963**, *39*, 1030.

[12] Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 877.

[13] Musso, G. F.; Magnasco, V. *Chem. Phys. Lett.* **1984**, *107* (6), 585.

[14] Skancke, A.; Straume, K. *Chem. Phys. Lett.* **1980**, *73*, 378.

[15] Lee, T.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III *Theor. Chim. Acta* **1989**, *75*, 81.

[16] Jursic, B. S. *Int. J. Quantum Chem.* **1996**, *57*, 213.

[17] For information about the theoretical background of the DFT formalism, see: Labanowski, J. K.; Andzelm, J. W. *Density Functional Methods in Chemistry*; Springer-Verlag: New York, Berlin, Heidelberg, London, Paris, Tokyo, Hong Kong, Barcelona, Budapest, 1991; Chapters 1 and 2.

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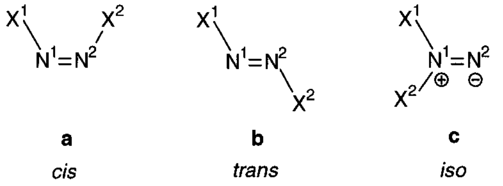

Compound	X^1	X^2
1a - c	F	F
2a - c	H	H
3a - c	F	H
4a - c	Cl	Cl
5a - c	Cl	H
6a - c	F	Cl

Figure 1. The different isomers of substituted diazenes.

studies to include the parent compound diazene **2** as well as various mono- and disubstituted derivatives (compounds **3**−**6**) in order to obtain a more detailed insight into the stability relationships of the different isomers. In the following discussion of our results, it is helpful to recognize that the size of the basis set as well as the calculational method employed has a significant effect upon the magnitude of the calculated electronic effects which in turn significantly influence the relative cis/trans stabilities obtained. The necessity of including electron correlation effects via MP2 or DFT methods such as B3LYP or BP86 is especially noteworthy.

Computational Methods

The semiempirical calculations were performed with MOPAC6/PC.[18] All semiempirical geometries were optimized at either the MNDO,[19,20] PM3,[21] or the AM1[22] levels without any symmetry restrictions. All ab initio and DFT calculations were performed using the Gaussian 94[23] program package. Geometries for ab initio calculations were initially optimized at the HF/6-31G* level, followed by optimization at the HF/6-311+G* level. The resulting HF/6-311+G* geometries were then employed as starting geometries for optimizations at the MP2/6-311+G*, B3LYP/6-311+G*, BP86/6-311+G*, BP86/6-311++G(3df,3pd) optimizations (systems containing hydrogen), and BP86/6-311++G(3df) (systems without hydrogen) levels of theory. We carried out CCSD(T)/6-311++G(3df) single-point calculations on the three isomers of difluorodiazene using B3LYP/6-311++G(3df) geometries in order to evaluate the capability of coupled cluster methods for the description of systems with coplanar lone electron pairs. All optimal structures found were characterized as energetical minima by calculation of their vibrational frequencies. Zero-point energies (ZPEs) of the HF results were scaled by 0.91.[24]

Results and Discussions

Difluorodiazene 1a−c. We begin our discussion with difluorodiazene **1** since this compound is, to date, the most intensively investigated diazene system. The cis form was experimentally determined in 1963 to be 3.1 ± 0.5 kcal/mol more stable than the trans form.[6] An ab initio bond orbital study employing small basis sets concluded in 1984 that the cis/trans energy relationships could be explained on the basis of localized and delocalized bond orbitals.[13] The authors emphasized, however, that their results are mainly of a qualitative nature. Nonetheless, their calculated structural data satisfactorily matched experimental data obtained from microwave spectroscopy[11c] as well as electron diffraction experiments.[11b] Despite their age, the accuracy of the experimental data is unusually good and they are of fundamental importance for more recent theoretical publications.[15] For the electron diffraction data, the error in the atomic distances was determined by the authors[11b] to be ±0.01 Å. The interatomic angles are estimated to be accurate to ±0.7°. Interestingly enough, the ab initio structural data reported in the literature[11−14] coincide much better with experimental structural data than do energetical calculations at the same level of theory. It has been shown[15] that the application of post SCF methods (MP2 perturbation theory in this case) is necessary in order to obtain energetical results that agree satisfactorily with the experimental data. In addition, the MP2 structural data agree somewhat better with experiment than the results of HF calculations reported in previous investigations.[13−15] A related discussion on the cis effect in substituted ethenes[10] is noteworthy in this context.

We optimized the three different isomers of difluorodiazene (see Figure 1) employing a variety of different methods. The results are summarized in Table 1. The semiempirical results vary considerably: AM1 predicts the cis isomer to be much too stable. PM3 agrees somewhat better with the experimental result. The discrepancy found for AM1 is not surprising since it is known that AM1 is not capable of correctly describing molecules containing adjacent lone pairs.[25] None of the semiempirical methods is capable of describing the iso form correctly. The HF calculation performed here shows a small preference for the trans isomer. This is in contradiction to the experimental results. Interestingly enough, the preference for the trans isomer at the HF level of theory increases with the complexity of the basis set. Employment of the relatively small 6-31G* basis yields a trans preference of 0.18 kcal/mol. Gradually increasing the size of the basis to 6-311+G* causes a corresponding increase in ΔE. Introducing electron correlation at the MP2/6-311+G* level of theory causes the cis isomer to become the more stable one, even though the cis/trans energy difference (1.5 kcal/mol) does not agree very well with the experimental value. A single-point calculation at the MP4/6-311+G*//MP2/6-311+G*

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[18] Wiedel, B.; Koch, R. QCMP 113. *QCPE Bull.* **1992**, *12*, 4 (based on MOPAC 6.0: Stewart, J. J. P. *QCPE Bull.* **1990**, 455).

[19] (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 777. (c) Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1983**, *4*, 158.

[20] (a) Thiel, W.; Voityuk, A. *Theor. Chim. Acta* **1992**, *81*, 391. (b) Thiel, W.; Voityuk, A. *Int. J. Quantum Chem.* **1992**, *44*, 807.

[21] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

[22] (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Dewar, M. J. S., Zoebisch, E. F. *J. Molec. Struct. (THEOCHEM)* **1988**, 180. (c) Dewar, M. J. S.; Jie, C. *J. Molec. Struct. (THEOCHEM)* **1989**, 187.

[23] Gaussian 94, Revision E.2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Al Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, J. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1995.

[24] Grev, R. S.; Jansen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1991**, *95*, 5128 and references therein.

[25] Anders, E.; Katritzky, A. R.; Malhotra, N.; Stevens, J. *J. Org. Chem.* **1992**, *57*, 3698.

Table 1. Structural and Energetical Data Calculated for the Isomers of Difluorodiazene at Various Levels of Theory

value[a]	AM1	PM3	HF[b]	MP2[b]	B3LYP[b]	BP86[b]	BP86[c]	exptl[e]
				cis				
R_{NN}	1.220	1.215	1.191	1.233	1.211	1.219	1.218	1.209
R_{NF}	1.356	1.350	1.326	1.382	1.395	1.421	1.402	1.409
α_{NNF}	124.2	119.0	114.6	114.6	115.3	116.0	115.8	114.4
ΔE^d	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
				trans				
R_{NN}	1.244	1.226	1.188	1.241	1.218	1.235	1.232	1.224
R_{NF}	1.348	1.342	1.326	1.377	1.387	1.409	1.402	1.398
α_{NNF}	113.0	112.1	107.5	105.3	105.7	104.8	104.9	115.5
ΔE^d	+10.56	+1.20	−1.80	+1.24	+1.84	+3.63	+3.29	+3.10
				iso				
R_{NN}	1.178	1.161	1.123	1.119	1.125	1.132	1.135	
R_{NF}	1.399	1.411	1.344	1.488	1.453	1.470	1.484	
α_{NNF}	131.1	129.9	129.2	132.1	131.1	131.4	131.4	
ΔE^d	+47.12	+19.37	23.47	+40.34	+11.73	+10.43	+8.54	

[a] Structural data are given in angstrom and degrees. Relative energies are reported in kcal/mol. [b] The 6-311+G* basis set was employed. [c] The 6−311++G(3df,3pd) basis set was employed. [d] Energy difference relative to the cis isomer (kcal/mol). [e] See lit. ref 11.

level increased the energy difference only slightly to 1.7 kcal/mol.

The B3LYP method yields results that do not differ much from MP2. Satisfactory results are obtained only when the BP86 functional is used in conjunction with a large basis set. The BP86/6-311+G* calculation yields a cis/trans energy difference of 3.6 kcal/mol. Increasing the size of the basis employed in BP86 calculation to 6-311++G(3df) results in a value of 3.3 kcal/mol which agrees quite well with the experimental value (3.1 ± 0.5 kcal/mol). To the best of our knowledge, this result is the most accurate one obtained to date.

Furthermore, we calculated the three isomers of difluorodiazene at the CCSD(T)/6-311++G(3df)//B3LYP/6-311++G(3df) level of theory following the proposal of Eckert and Rauhut for the treatment of systems containing coplanar lone electron pairs.[26] With this method, we obtained a cis preference of 1.1 kcal/mol. On this level of theory, the iso conformer is predicted to be 41.2 kcal/mol less stable than the cis isomer. This result shows clearly that even the coupled cluster method is not capable of describing substituted diazenes correctly.

A comparison of structural data calculated for the cis and trans isomers with experimental values shows that all methods describe the N═N bond in both isomers accurately to within ca. 0.03 Å. Interestingly, the N═N bond length calculated at the HF level is slightly too short. Inclusion of electron correlation via the MP2 method results in a N═N bond length that is somewhat too long. This is most probably due to the fact that the MP2 method tends to overestimate electronic repulsion.[27] The best match between experiment and theory was found for the density functional methods B3LYP and BP86.

A much stronger dependence upon the computational method employed is found for the N−F bond length. Methods that do not include electron correlation (AM1, PM3, HF) result in values for the N−F bond length that are 0.05−0.07 Å too short as compared with experiment. Inclusion of electron correlation via the MP2 or B3LYP method improves things considerably, although the results are still slightly too short. The BP86 method, on the other hand, yields values that are slightly too long. Only at the relatively high BP86/6-311++G(3df,3pd) level do the computational results lie within experimental error bars.

The semiempirical methods are not capable of accurately reproducing the NNF bond angle in the cis isomer. All of the ab initio and DFT methods yield acceptable results with the deviation from experiment being largest for the BP86 method. However, none of the methods investigated here are capable of reproducing the NNF bond angle in the trans isomer. All ab initio and DFT values are 8−10° too small.

Diazene 2. A recent field of biochemistry is mechanistic investigations of the enzymatic reduction of molecular nitrogen to ammonia by soil microorganisms.[28] The most endothermic step in this electron transmission chain is the first reaction step, which leads to diazene. This has been successfully simulated by Sellmann et al. using model compounds for the enzyme nitrogenase.[29,31] For a long time now, a demand of chemical technology has been to find an ammonia synthesis which runs under milder conditions as well as having a higher yield than the classical Haber−Bosch method. For both the biochemical research and the search for technical applications, it is important to have some knowledge about the electronic and structural properties of diazenes in order to find appropriate systems for the nitrogen fixation.

The number of experimental publications dealing with diazene itself is small, although its existence was postulated more than 100 years ago.[30] Near-ultraviolet absorption investigations of diazene in the gas phase showed that the trans isomer is the most stable one.[31] Trans diazene has also been detected in the condensed phase at temperatures lower than −168 °C.[32] The structure of diazene in solution remained an enigma for quite a long time until Sellmann and Hennige managed to show in 1997,[33] 105 years after its first appearance in the scientific literature, that the trans-isomer is the most stable one.

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(26) Eckert, F.; Rauhut, G. *J. Am. Chem. Soc.* **1998**, *120*, 13478.

(27) Foresman, J. B.; Frisch, M. J. *Exploring Chemistry with Electronic Structure Methods − A Guide to using Gaussian*; Gaussian Inc.: Pittsburgh, PA, 1993; p 216.

(28) Cowan, J. A. *Inorganic Biochemistry−An Introduction*; Wiley, VCH: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, 1997; p 233.

(29) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem.* **1989**, *101*, 1244.

(30) Thiele, W. *Liebigs Ann. Chem.* **1892**, *271*, 127.

(31) Back, R. A.; Willis, C.; Ramsay, D. A. *Can. J. Chem.* **1974**, *52*, 1006.

(32) Wiberg, N.; Fischer, G.; Bachhuber, H. *Chem. Ber.* **1974**, *107*, 1456.

(33) Sellmann, D.; Hennige, A. *Angew. Chem.* **1997**, *109*, 270.

Table 2. Relative Energies of the Different Conformers of Diazene 2 and the Dependence on the Computational Method Employed

method	Δ*E*(cis−trans)	Δ*E*(iso−trans)
AM1	+0.9	+24.2
PM3	+5.1	+12.2
HF/6-311+G*	+7.7	+17.6
MP2/6-311+G*	+7.5	+25.4
MP2/6-311++G**	+6.7	+27.3
B3LYP/6-311+G*	+6.5	+19.7
QCISD/6-311++G**	+6.4	+23.8
QCISD(T)/6-311++G**	+6.3	+24.7
BP86/6-311+G*	+6.0	+19.2
B3LYP/6-311++G(3df,3pd)	+5.0	+20.5
B3PW91/6-311+G(3df,3pd)	+5.1	+20.8
BP86/6-311++G(3df,3pd)	+4.6	+20.4

Table 3. Relative Stabilities Calculated at Various Computational Levels of the Isomers of the Halogen-Substituted Diazenes 3−6

system[a]	AM1	PM3	MNDO	HF[b]	MP2[b]	B3LYP[b]	BP86[b]	BP86[c]
				fluorodiazene **3**				
cis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans	+5.5	−2.2	+1.1	−1.0	+1.4	+3.0	+4.2	+3.6
iso	+37.3	+15.8	+48.1	+17.5	−1.7	+1.3	+3.2	+4.3
				dichlorodiazene **4**				
cis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans	+14.3	−0.3	+2.1	−3.4	+3.1	+4.5	+7.4	+6.8
iso	+45.1	+17.6		+15.4		+11.3	−6.2	−11.7
				chlorodiazene **5**				
cis	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
trans	+7.4	−1.8	+1.1	−1.4	+1.5	+3.6	+4.8	+4.3
iso	+30.0	12.8		*d*	−1.1	+3.3	+3.0	+0.2
				chlorofluorodiazene **6**				
cis	0.0	0.0		0.0	0.0	0.0	0.0	0.0
trans	+11.6	+0.3		−1.9	+2.4	+3.5	+5.7	+5.2
iso	+52.8	+21.6		+9.4	+6.1	+6.5	+3.1	+5.2

[a] Energy differences are relative to the *cis* isomer and given in kcal/mol. [b] The 6-311+G* basis set was employed. [c] The 6-311++G/3df/3pd) basis set was employed. [d] The separate molecules N_2 and HCl are found for the HF/6-311+G* level of theory.

The small size of diazene enabled us to study the convergence of the cis/trans energy relationships by successively raising the level of theory employed. We therefore carried out calculations for diazene using a wide range of theoretical levels (Table 2).

All calculational methods agree with experiment in that the trans isomer is the most stable one. The relative stability of the trans isomer converges smoothly from 7.7 kcal/mol (HF/6-311+G*) to 4.6 kcal/mol (BP86/6-311++G(3df,3pd)) as the computational method is improved. It is not surprising that the result obtained at the MP2 level is slightly larger than that calculated using the B3LYP method with a comparable basis set since the MP2 method slightly overestimates lp/lp repulsion.[26] Taking the results we obtained for the difluorodiazene system, the BP86/6-311++G(3df,3pd) calculation shows an overestimation of the stability of the cis isomer of 0.2 kcal/mol as compared to experiment. Assuming that the stability of the cis isomer is also overestimated for diazene, the true value probably lies between the B3LYP/6-311++G(3df,3pd) value (5.1 kcal/mol) and the BP86/6-311++G(3df,3pd) value (4.6 kcal/mol). A best estimation for the energy difference would thus be ca. 4.9 kcal/mol. The destabilization of the iso conformer appears to be caused by a polarization of the NN double bond which leads to a rather large charge separation between the nitrogen atoms.

Due to the lack of experimental structural data for comparison, we do not discuss the effect of the computational method upon the individual parameters. The structural data obtained at the BP86/6-311++G(3df,3pd) level agree very well, however, with the G2[34] results published by Pople and Curtiss,[35] thus indicating that the results obtained here are among the most accurate ones available to date.

Summarizing our most important findings, we conclude that the density functional methods BP86 and B3LYP deliver reliable results when middle-sized (6-311+G*) to large basis sets are employed. The cis/trans energy difference calculated at the B3LYP and BP86 level is assumed to be dominated by the destabilizing electrostatic repulsion of the adjacent nitrogen lone pairs which are located on the same side of the molecular plane in the cis isomer.

Substituted Diazenes 3−6. The halogen-substituted diazenes **3**−**6**, analogous to difluorodiazene **1** and in contrast to diazene **2**, show a significant cis effect (Table 3).

It is absolutely necessary, however, to employ a correlated method for the determination of the relative energies of the different isomers. Although the semiempirical methods AM1 and PM3 in the most cases succeed in describing the relationships between structure and energy, they are unreliable for the systems discussed here. In general, PM3 shows a preference for the trans isomer. The magnitude of the cis preference calculated by AM1 is again on average much too large probably due to an inadequate description of the interaction of the neighboring lone pairs.[25] None of the semiempirical methods come even close to being able to describe the relative energy of the iso isomer. The HF method is also unsatisfactory since it yields a clear trans preference. Among the correlated methods, MP2 reliably delivered the smallest cis preference for all compounds studied here. As was already discussed for difluorodiazene **1**, this is not surprising and is due to a simple overestimation of the cis lp/lp repulsion.[36] Going from MP2 to B3LYP and then to the BP86 method causes a steady increase in the calculated cis preference. The only exception to this is found for the BP86 method itself. An increase in the size of the basis set employed from 6−311+G* to 6-311++G(3df,3pd) causes a slight decrease in the cis preference. This appears to be a general characteristic for diazenes with the experimental value most probably lying somewhere in between.

The most significant difference between the fluorinated and the chlorinated diazenes is a higher cis preference in the chlorinated compounds due to a decreased halogen−halogen repulsion. The larger N−Cl bond length results in a larger halogen−halogen nonbonding distance in the cis isomer as compared to difluorodiazene. In addition, the partial charge calculated for chlorine is smaller than for fluorine. These results agree with the findings reported for 1,2-dihaloethylenes which also show an increasing cis effect with the increase of the atomic weight of the substituents.[10]

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(34) Curtiss, L. A.; Raghavacharari, G. W.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(35) Pople, J. A.; Curtiss, L. A. *J. Chem. Phys.* **1991**, *95*, 4385.

(36) Foresman, J. B.; Frisch, M. J. *Exploring Chemistry with Electronic Structure Methods*; Gaussian Inc.: Pittsburgh, PA, 1993; p 114.

Table 4. Selected Structural Parameters and Bond Orders for Compounds 2–6 Calculated at the BP86/6-311++G(3df,3dp) Level of Theory

system[a]	$r_{N=N}$	$BO_{N=N}$	r_{N-X1}	BO_{N-X1}	r_{N-X2}	BO_{N-X2}	α_{NNX1}	α_{NNX2}
				diazene **2**				
cis	1.246	2.069	1.051	0.872	1.051	0.872	118.9	112.9
trans	1.249	2.067	1.045	0.864	1.045	0.864	106.4	106.4
iso	1.213	2.003	1.062	0.753	1.062	0.753	110.6	110.6
				fluorodiazene **3**				
cis	1.900	2.245	1.541	0.750	1.040	0.800	111.0	115.8
trans	1.208	2.122	1.463	0.852	1.038	0.806	107.7	105.2
iso	1.133	2.545	1.698	0.421	1.028	0.744	126.4	143.5
				dichlorodiazene **4**				
cis	1.240	2.136	1.831	0.895	1.831	0.895	123.0	123.0
trans	1.219	2.045	1.808	0.911	1.808	0.911	108.2	108.2
iso	1.132	2.493	1.950	0.601	1.950	0.601	103.2	103.2
				chlorodiazene **5**				
cis	1.191	2.234	1.959	0.812	1.040	0.797	115.4	119.7
trans	1.212	2.104	1.863	0.937	1.043	0.792	111.4	106.0
iso	1.430	2.445	2.133	0.490	1.031	0.740	128.6	136.4
				chlorofluorodiazene **6**				
cis	1.206	2.146	1.786	0.930	1.472	0.825	122.2	116.8
trans	1.227	1.991	1.773	0.981	1.443	0.877	108.5	104.9
iso	1.133	2.504	1.789	0.796	1.603	0.525	135.6	125.2

[a] Structural parameters are given in angstroms and degrees. Bond orders are reported in measures of electron pairs.

When both fluorine and chlorine are present in the same molecule (compound **6**), one would expect an almost additive contribution in the electronic behavior of each halogen substituent. This is indeed the case with the calculated cis stability for F–N=N–Cl lying almost in the middle between the relative energies obtained for the symmetrically substituted diazenes (F–N=N–F, 3.3 kcal/mol; F–N=N–Cl, 5.2 kcal/mol; Cl–N=N–Cl, 6.8 kcal/mol; BP86/6-311++G(3df,3pd) level).

All diazenes considered here show a clearly recognizable N=N bond shortening in the cis isomer as compared to the trans (Table 4). This is due to the presence of *negative hyperconjugation*, as will be discussed in the next section. The bond length shortening is slightly larger for the chlorinated as compared to the fluorinated compound. In accord with the change in the bond length, a slightly larger NN bond order is calculated for the cis compound (Table 4). In addition, a considerable lengthening of the NX bond is present. This again indicates the presence of negative hyperconjugation.

Steric hindrance in the cis compound is compensated for by an increase in the NNX bond angle. This increase is ca. 12° for diazene itself and the symmetrically substituted compounds **1** and **4**. For monosubstituted diazenes, the increase in the NNX bond angle is significantly smaller—only about 4°. A smaller NNX angle indicates the presence of a stabilizing electrostatic interaction in these unsymmetrical diazenes which contributes to the cis preference found (see Figure 2). If a symmetrically substituted diazene is considered, the electrostatic interaction is repulsive and joins the steric effects in widening the NNX bond angle.

The iso conformer of halogen-substituted diazenes is a quasi-ionic system and is generally the least stable of the three isomers investigated here. The NN bond in the iso conformer is extremely short and possesses a partial triple bond character ($BO_{NN} \approx 2.5$). The N–X bond is considerably elongated as compared with the other two isomers and shows a weakened bond order ($BO_{NX} \approx 0.5$). The atomic charges are highly polarized in the iso conformer (see Table 5). The halogen possesses a large negative charge and the neighboring nitrogen is considerably positively charged.

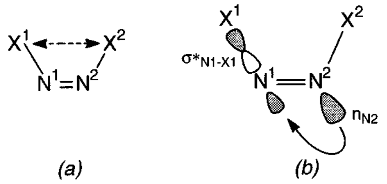

Figure 2. (a) Electrostatic interaction between the two substituents in the cis isomers. The interaction is repulsive for symmetrical and attractive for asymmetrical systems. (b) Negative hyperconjugation in substituted cis diazenes. The n_{N2} orbital partially delocalizes into the σ^*_{N1-X1} orbital.

Electronic Interactions in Diazenes. The shortening of the NN bond length calculated for the cis isomer coupled with the lengthening found in the N–X^1 bond indicates the presence of negative hyperconjugation in the series of diazenes investigated here. This corresponds to the partial delocalization of the nitrogen lone pair orbital n_{N1} into the σ^* orbital of the neighboring N–X^1 bond (σ^*_{N-X1}).[37,38] This donor/acceptor (d/a) interaction [$n_{N2} \rightarrow \sigma^*_{N-X1}$] is only present in the cis isomer (Figure 2).

Negative hyperconjugation results in a larger occupancy of the σ^*_{N-X} orbital in the cis isomer whereas the occupancy of the lone electron pair orbital n_N decreases (Table 5). This leads to a slight increase in the negative charge calculated for X.[39]

As the electronegativity of X increases (F > Cl > H), a depopulation of the n_N lone pair orbital in the trans isomer is also present, although to a significantly lesser extent. The depopulation calculated for the trans isomer is mainly due to an inductive effect. A halogen substituent (especially fluorine) withdraws a certain amount of electron density from the N–X bond and the lone electron pair on nitrogen regardless of their positions in the molecule. The resulting NN bond polarization strengthens the tendency of the lone pair of the unsubstituted N atom to delocalization into the σ^*_{N-X} acceptor bond orbital, assuming a cis conformation is present. To evaluate the influence of the substituents X on the magnitude of the negative hyperconjugation present, we graphed the difference Δn_N in the occupation number n of the lone pair orbital on nitrogen relative to the trans isomer ($\Delta n_N = n_{N,cis} - n_{N,trans}$) versus the occupancy difference Δn_{σ^*} calculated for the σ^*_{N-X} orbital (Figure 3). If the depletion in the lone pair orbital on nitrogen is mostly due to negative hyperconjugation, one should see a linear correlation diagram. As can be seen from Figure 3, this is nearly the case. The direct proportionality found emphasizes the interaction of the two orbitals. The linear

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(37) For an introduction and experimental applications, compare: (a) Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; John Wiley & Sons: New York, Chichester, Brisbane, Toronto, Singapore, 1991. (b) Juaristi, E. *Conformational Behavior of Six-Membered Rings: Analysis, Dynamics, and Stereoelectronic Effects*, VCH Publishers: New York, 1995. (c) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, New York, Sydney, Paris, Frankfurt, 1984.

(38) Hehre, W. J.; Radom, L.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, Chichester, Brisbane, Toronto, Singapore, 1986; p 356.

(39) For recent experimental applications, see: Anders, E.; Opitz, A.; Wiedel, B.; Görls, H. *J. Org. Chem.* **1999**, *64*, 3113.

Table 5. Selected Atomic Charges and Occupancy Numbers Calculated at the BP86/6-311++G(3df,3dp) Level of Theory

system[a]	q_N[b]	q_{X1}	q_{X2}	occ.(lp_{N1})	occ.(lp_{N2})	occ.(σ^*_{NX1})	occ.(σ^*_{NX2})
			difluorodiazene **1**				
cis	0.212	−0.212	−0.212	1.909	1.909	0.269	0.269
trans	0.198	−0.198	−0.198	1.944	1.944	0.055	0.055
iso	0.448/0.000	−0.224	−0.224		1.994	0.292	0.292
			diazene **2**				
cis	−0.273	0.273	0.273	1.963	1.963	0.039	0.039
trans	−0.295	0.295	0.295	1.985	1.985	0.027	0.027
iso	−0.351/−0.222	0.289	0.289		1.987	0.121	0.121
			fluorodiazene **3**				
cis	0.246/−0.262	−0.347	0.362	1.975	1.791	0.262	0.041
trans	0.213/−0.297	−0.276	0.362	1.993	1.915	0.159	0.017
iso	0.007/ 0.053	−0.473	0.413		1.980	0.269	0.062
			dichlorodiazene **4**				
cis	−0.083	0.083	0.083	1.857	1.857	0.228	0.228
trans	−0.115	0.115	0.115	1.976	1.976	0.108	0.108
iso	−0.071/ 0.049	0.011	0.011		1.944	0.269	0.269
			chlorodiazene **5**				
cis	0.007/0.230	−0.132	0.356	1.937	1.766	0.281	0.051
trans	−0.077/−0.283	0.006	0.354	1.990	1.918	0.163	
iso	−0.071/0.049	−0.320	0.412		1.982	0.609	0.067
			chlorofluorodiazene **6**				
cis	0.240/−0.144	−0.251	0.155	1.891	1.870	0.170	0.128
trans	0.197/−0.160	−0.221	0.184	1.990	1.959	0.103	0.046
iso	0.109/0.043	−0.332	0.180		1.994	0.461	0.220

[a] All charges and occupancy numbers are given in electrons. [b] Given in the order N1, N2.

regression function we found is

$$\Delta_{cis-trans}occ.(\sigma^*_{N-X}) = -0.919\Delta_{cis-trans}occ.(n_N) + 0.010$$

According to Figure 3, the acceptor ability for a σ^*_{N-X} orbital is ordered as follows:

$$N-Cl > N-F > N-H$$

If one takes the σ^*_{N-Cl} orbital as the standard, the donor strength of the n_N lone pair orbitals as a function of the substituent X can be ordered as follows:

$$H > Cl > F$$

As expected, the donor strength of the lone electron pair coincides with the electronegativity of the substituent. The higher the electronegativity of a substituent, the lower is the related donor strength.

The results obtained here indicate that the cis preference found for substituted diazenes can be interpreted as the sum of three different electronic interactions:

(1) Negative hyperconjugation. Partial delocalization of the lone pair on nitrogen (n_{N2}) into the σ^*_{N1-X} orbital leads to a significant stabilization of the cis form.

(2) Electrostatic interaction between the two substituents X^1 and X^2. This interaction stabilizes the cis form of the unsymmetric and destabilizes that of symmetric diazenes.

(3) Electrostatic interaction between the lone electron pairs on adjacent N atoms. This interaction destabilizes the cis conformer.

In light of these results and recognizing that the negative hyperconjugation present in diazene itself ($X^1 = X^2 = H$) is very small, it is not surprising that diazene prefers a trans conformation. All other diazenes studied here show a clear cis preference.

Conclusion

We investigated the cis/trans energy relationships of halogen-substituted diazenes in detail and found an explanation for the observed cis effect. This phenomenon, reported in the literature so far only for difluorodiazene, is valid for all halogen-substituted diazenes. Negative hyperconjugation as discussed above is the main reason for the cis stabilization. A further factor influencing the cis/trans energy relationship is the electrostatic interaction between the substituents in the cis isomer. This interaction is repulsive for symmetrically substituted and attractive for asymmetrically substituted systems. The acceptor strength of the σ^*_{N-X} orbitals in the cis isomers correlates directly with the σ^*_{N-X} orbital energy. The

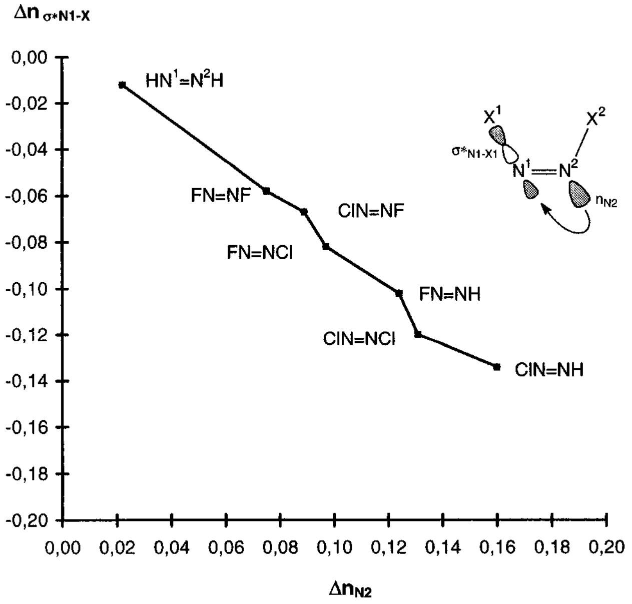

Figure 3. The decrease in the occupation difference (trans−cis) of the σ^*_{N-X} orbital (Δn_{σ^*N-X}) orbital plotted as a function of the increase in the occupation difference (trans−cis) of the lone pair orbital on nitrogen (Δn_N), calculated at the BP86/6-311++G(3df,3pd) level of theory. For the unsymmetrical substituted systems, the N^2 lone pair is the donor and the σ^*_{N1-X1} is the acceptor.

donor strength of the n_N orbitals (lone pair orbitals on nitrogen) corresponds with the electronegativity of the adjacent substituent X.

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