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Computational Methods in Organic Thermochemistry. 4. Enthalpies and Gibbs Energies of Formation of the *cis*- and *trans*-Diazenes

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The enthalpies and Gibbs energies of formation are examined for over 100 aliphatic *cis*- and *trans*-diazenes using the G3, G3(MP2), and CBS-QB3 model chemistries for compounds ranging from two to ten heavy atoms. The values computed using bond separation reactions were corrected to compensate for the presence of higher energy conformers. Comparison of several homologous and isomeric series shows that alkene thermochemistry is not an adequate model for the diazenes (HN=NH) as the group equivalents of the latter differ significantly from those of the former when they are adjacent or one atom removed from the nitrogen−nitrogen double bond. Methylene insertion adjacent to the double bond is less exothermic for the diazenes than it is for the alkenes whereas the same insertion one carbon atom away from the double bond is more exothermic than that observed for the alkenes. The data argues that molecular modeling programs parametrized using existing experimental data will need to be recalibrated.

Introduction

Diazene is a simple nitrogen compound whose oxidation level is between that of dinitrogen and hydrazine.

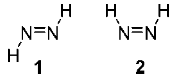

Figure 1

It has been suspected or identified as a substrate of the nitrogenase enzymes used in the biological fixation of nitrogen[1−7] and postulated as an intermediate in the industrial fixation of nitrogen.[8,9] Also known as *diimide*, it is used as a reducing agent in laboratory reductions[10] and has been suggested for use in chemical hydrogen storage systems.[11]

Values for the thermodynamic properties of **1** are available from the Computational Chemistry Comparison and Benchmark DataBase[12] and those for **2** are available from the NIST Webbook.[13] Using properties of simple molecules such as these in isodesmic bond separation reactions (eq 1), we have found that ab initio computation affords reliable enthalpies and Gibbs energies of formation for the hydrocarbons[14] and functionalized derivatives.[15] With most functional groups we have found the G3/G3(MP2), G3B3/G3(MP2)B3, and CBS-QB3 procedures to be within four, and in many instances, two kJ/mol of experimental values. The diazenes were an exception to this with deviations as large as 20 kJ/mol.

$$CH_3CH_2N{=}NCH_2CH_3 + {}_2CH_4 + {}_2NH_3 \rightarrow {}_2CH_3CH_3 + {}_2CH_3NH_2 + HN{=}NH \qquad (1)$$

$$CH_3CH_2N{=}NCH_2CH_3 \rightarrow 4C(g) + 10H(g) \qquad (2)$$

In Table 1, we tabulate the enthalpy of formation of some straight chain monoalkyl diazenes, *cis* and *trans*, computed using both atomization (eq 2) and bond separation reactions. Examination of the data shows that the values differ from each other by a constant factor. Given that there is good agreement between the bond separation and atomization enthalpies of formation for the alkyl amines, the only difference between the amines reported in our earlier paper[15] and those results shown in Table 1 is the experimental value of the corresponding diazene itself. This argues that the values reported in refs 12 and 13 may be in error.

TABLE 1: Comparison of Standard State Enthalpies of Formation[a] Computed Using Bond Separation and Atomization Methods for Simple *cis*- and *trans*-Diazenes.

	BSE[b]	atom[c]	ΔΔ*H*
trans-Diazenes			
methyl diazene	186.7	181.9	4.8
ethyl diazene	159.4	154.6	4.9
propyl diazene	138.8	133.8	4.9
isopropyl diazene	123.8	118.8	4.9
butyl diazene	117.4	112.4	5.0
isobutyl diazene	110.3	105.3	5.0
cis-Diazenes			
methyl diazene	183.4	198.8	−15.5
ethyl diazene	155.6	170.9	−15.4
propyl diazene	134.7	150.0	−15.3
isopropyl diazene	119.5	134.7	−15.3
butyl diazene	113.3	128.5	−15.2
isobutyl diazene	105.5	120.7	−15.2

[a] kJ/mol. [b] Computed by bond separation reactions, eq 1. [c] Computed by atomization of the diazene (eq 2).

Regardless of the model chemistry employed and even if we correct for the presence of higher energy conformers,[16] only five of the 11 alkyl diazenes for which enthalpy values are cited in the literature are within 4 kJ/mol of those values, and of the remaining six, none are within 8 kJ/mol. It is important to note that the values cited for the simple methyl and ethyl diazenes which are included in the aforementioned eleven compounds were not determined by either calorimetry or other experimental data, rather they were derived from the enthalpies of homologues. Thermodynamic properties of these substances reported in tabulated databases can be traced to a pair of papers by

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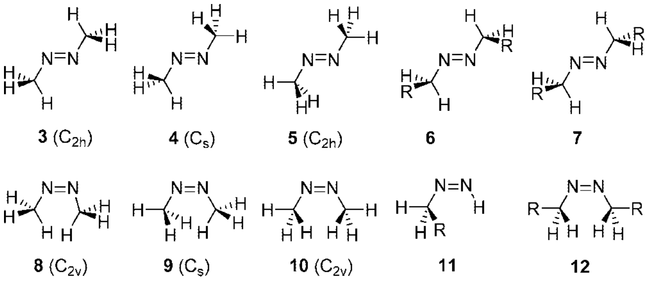
Rossini et al.[17,18] For those values which Rossini derived from the experimental values, there is a consistent 8−13 kJ/mol difference between reported and computational results. Even those diazenes whose enthalpies have been determined by Engel et al.[19,20] by calorimetric experiments differ from our computational results by more than the 8 kJ/mol that we have defined as our limit for acceptability. As we were in the process of organizing our results for the organic functional groups,[15] it was clear that the diazenes would need to be examined separately and critically in order to resolve the discrepancies. In the paragraphs that follow in this introduction, we will review the literature and from the variety of data, experimental and computational, draw a best conclusion for the enthalpies of the parent compounds, *cis*- and *trans*-diazene. On that foundation, we will then discuss the results of best practice computations and examine the reliability of the tenets that have been used to determine the values reported in the literature.

Nelsen reported the decomposition of 1,2,3,6-tetrahydropyridazine derivatives, isolating both the *cis*- and *trans*-dimethyldiazenes.[21] He observed a difference in product distribution that was accounted for by a difference in thermodynamic stability that would be approximately 20 kJ/mol. Reasoning that the difference between *cis*- and *trans*-2-butene is significantly less than this value, he attributed the difference to electronic factors. Combining the $\Delta\Delta H$ for the *cis*- and *trans*-diazenes from Table 1 gives ~20 kJ/mol, and this suggests that the differences observed by Nelsen may indeed be steric.

As a prelude to a high level computational study of both the *trans* (**1**) and *cis* (**2**) forms, Martin and Taylor have thoroughly reviewed previous experimental and computation work on these compounds.[22] The NIST value of 211.86 ± 10 kJ/mol for *trans*-diazene[12] references a value given by Gurvich.[23] The value given by Foner and Hudson[24] in their initial report of diazene is 203.76 kJ/mol. In a later paper,[25] they gave a slightly larger value of 212.1 kJ/mol. Both values are within the error bars of the NIST value and the latter is nearly identical. More recent values, include 188.3 kJ/mol by photoionization mass spectrometry[26] and 204.1 kJ/mol by vacuum-ultraviolet photolysis.[27] Several values are available from the computational literature. Pople and Curtiss[28] obtained a value of 207.5 kJ/mol using G2 atomization energies, Walch[29] obtained a value of 212.5 kJ/mol using CASSCF/multireference contracted CI calculations, and Martin and Taylor determined a value of 205.85 kJ/mol.[22] The latter employed a very rigorous coupled cluster method with basis sets as large as [7s6p5d4f3g2h/5s4p3d2f1g] and extrapolated toward the 1-particle basis set limit. The values obtained, experimental and computational, tend to cluster in two regions: ~205 and ~212 kJ/mol. Our own G3 atomization enthalpy for *trans*-diazene, 206.1 kJ/mol, is very close to the experimental value given in ref 27 and to the computed value from Martin and Taylor.[22]

The NIST Webbook value of 212.97 kJ/mol for the *cis* isomer references the JANAF tables[30] which in turn reference an early paper by Foner and Hudson.[31] This is nearly identical to the value given by the same authors in ref 25 and the enthalpy given for the *trans* isomer. It is worth noting that these workers give no data in either of these papers to confirm the structure of the compound isolated as either *cis* or *trans*. Computational estimates of the formation enthalpy are nonexistent; rather workers who have studied the *trans*/*cis* isomers have focused on the isomerization energy. These vary from 20.9 to 22.2 kJ/mol.[22,32−34] The difference between our *cis*- and *trans*-diazenes, 22.2 kJ/mol, is consistent with the computational results cited above. Hence we will use as experimental values the 204.1 kJ/mol value given in ref 27 for *trans*-diazene and 226.3 kJ/mol based on the *cis*−*trans* isomerization energy from our calculations and those cited above.

SCHEME 1: Conformations of the Dimethyldiazenes



The structures of *cis*- and *trans*-dimethyldiazene have been examined rigorously by Hu and Schaefer.[35] They showed that *trans*-dimethyl diazene has a structure (**3**) analogous to the local minimum for *trans*-2-butene. Structures **4** and **5** have one and two imaginary frequencies, respectively, and homologues (**6** and **7**) will have the alkyl group, R out of plane, all of which is analogous to *trans*-2-butene. The epimers **6** and **7** are within $^{1}/_{10}$th kJ/mol in energy of each other.

In contrast, structure **8** corresponding to *cis*-2-butene, has two imaginary frequencies and the single rotamer **9** has one. The local minimum for this compound is **10**. The monoalkyl diazenes (**11**) resemble the alkenes in that the alkyl group lies out of the plane. Because of steric hindrance, dialkyl homologues are different from the *trans* compounds in that the alkyl groups are either in plane as shown in structure **12** or nearly so.

Methods

We have employed the Gaussian 98[36] suite of programs and more recently, Gaussian 03[37] to determine all structures and energies reported here. Normally, the rigorous G3, G3B3, and CBS-QB3 model chemistries are limited to a maximum number of seven heavy atoms in compounds having no symmetry, however, the presence of unsaturation increases the number of heavy atoms that can be calculated. Apparently the CBS-QB3 method benefits more from this than the G3 as we are able to calculate diazenes with nine and ten heavy atoms whereas very few of the those with eight heavy atoms could be calculated with the G3 model chemistry without the use of 64 bit computers.[38] This paper reports thermodynamic properties for over twenty compounds having ten or more heavy atoms, thus it is very possible to compute these properties at very high levels for midsize molecules.

In some instances, there were difficulties optimizing sterically hindered molecules using the CBS-QB3 method. It would become locked in an infinite loop, close to a final structure, but not able to reach it. In these instances, stretching of the carbon−carbon bond close to the congested center allows the optimization to reach a final conclusion.[39] In two cases, there was significant divergence between the calculated G3 or G3(MP2) enthalpies and those obtained with CBS-QB3. In these cases, using the HF/6−31G* optimized geometry as input for the latter calculation allowed us to achieve concurrence between all three model chemistries. Apparently, the Hartree−Fock optimization is better able to resolve the conflicts between repulsive groups in the *cis* isomers.

The absolute energies were converted into standard state enthalpies and Gibbs energies using bond separation energies as described in our initial work and illustrated in eq 1.[14] In previous papers, it has been our practice to cite secondary

TABLE 2: Comparison of the Enthalpies and Gibbs Energies[a] Corrected from the Global Conformational Minimum vs Those Computed by Explicit Computation of All Conformers

	G3 enthalpies		G3MP2 enthalpies		CBS-QB3 enthalpies	
	predicted[b]	computed[c]	predicted[b]	computed[c]	predicted[b]	computed[c]
trans Isomers						
ethyl diazene	153.1	152.8	153.7	153.4	153.6	153.3
propyl diazene	133.1	132.1	133.7	132.8	133.7	132.7
butyl diazene	112.3	111.2	113.1	112.0	113.2	112.1
pentyl diazene	91.4	90.0	92.4	90.9	92.4	90.8
cis Isomers						
ethyl diazene	169.5	169.1	170.3	169.9	170.3	169.9
propyl diazene	149.2	147.3	150.2	148.3	150.3	148.4
butyl diazene	126.5	126.4	127.6	127.5	127.8	127.7
pentyl diazene	105.4	105.2	106.7	106.5	106.8	106.2
mean absolute devation	0.8		0.8		0.9	
standard deviation		0.7		0.6		0.6

	G3 Gibbs energies		G3MP2 Gibbs energies		CBS-QB3 Gibbs energies	
	predicted	computed	predicted	computed	predicted	computed
trans Isomers						
ethyl diazene	239.8	239.7	240.4	240.2	240.3	240.1
propyl diazene	248.7	247.8	249.4	248.5	249.3	248.3
butyl diazene	256.9	256.5	257.8	257.4	257.8	257.4
pentyl diazene	265.0	265.3	266.0	266.3	266.0	266.3
cis Isomers						
ethyl diazene	256.3	256.5	257.1	257.3	257.2	257.3
propyl diazene	265.0	263.5	266.0	264.5	266.2	264.6
butyl diazene	271.9	272.3	273.0	273.4	273.2	273.6
pentyl diazene	279.8	281.0	281.1	282.3	281.1	283.0
mean absolute devation	0.6		0.6		0.7	
standard deviation		0.5		0.5		0.7

[a] kJ/mol. [b] Corrected global conformational minimum. [c] Explicit computation of all gauche conformations.

sources of experimental values, particularly those that can be accessed from the Internet. In the current situation, there are so few available, that it is as convenient to cite the primary sources.

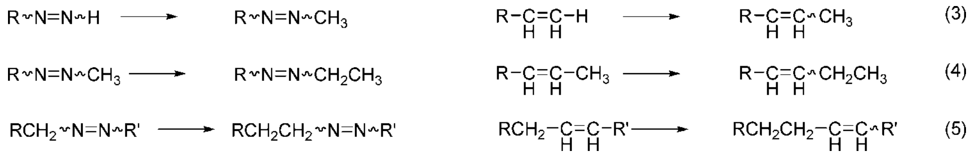
Results and Discussion

Correction for Multiple Conformations. In our earlier papers,[14,16] we reported that in place of computing all conformers of a molecule, a simple series of corrections for the enthalpies and Gibbs energies were sufficient to give reliable values. For the enthalpies, a constant 0.6 kJ/mol per rotatable bond was added to the computed enthalpy regardless of proximity to any functionality.[16] We define as rotatable, any carbon−carbon bond whose rotation affords a different conformer. The Gibbs energies were corrected by subtracting 1.2 kJ/mol for each rotatable carbon−carbon bond.[14] The exception to the aforementioned value occurs when the rotatable bond is adjacent to a functional group such as a double bond or heteroatom. The correction for these cases is dependent upon the nature of the functionality and these are discussed thoroughly in references[14] and.[15] The corrected values agree well with the energies derived by computing all conformers. In the cited papers, it was found that errors resulting from omission of g^+g^- conformers were negligible until there were nine to ten carbon atoms in the chain.

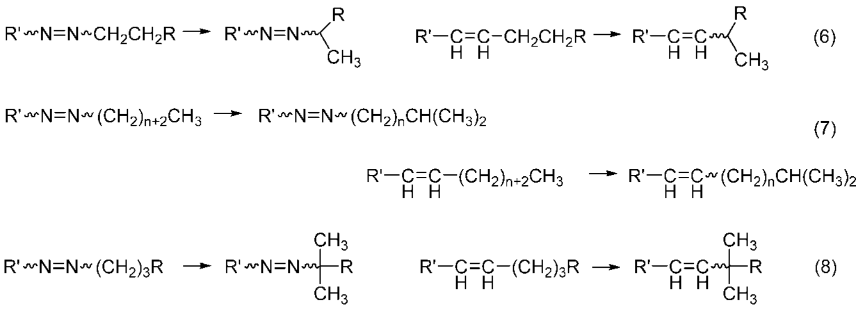
The difficulty in determining the validity of the corrections for the project in hand is that there are no experimental entropies upon which to base a Gibbs energy calculation for comparison of the computed data. Hence, for a handful of compounds, we have explicitly calculated all conformations and computed a composite enthalpy and Gibbs energy for each. For each we examined the energy changes that accompanied the inclusion of all conformations and again only those in which the rotation was around the bond adjacent to the diazene moiety.[40] Based on these results, it appears that the protocol for computing the enthalpy corrections is also valid for the diazenes. For Gibbs energies, examination of a number of compounds including both *cis*- and *trans*-diazenes and those substituted with a methylene (CH_2) and methyne (CH) show that rotation of a bond adjacent to the nitrogen−nitrogen double bond results in an energy lowering of 1.9 kJ/mol. This is true for either the *cis*- or *trans*-monosubstituted compounds. For the disubstituted diazenes, the correction is taken twice for the *trans* compounds, but not for the *cis*. In the latter, steric congestion renders the rotamers too high in energy to make any significant contribution to the Gibbs energy. It appears that the 1.2 kJ /mol for rotatable bonds away from the functional group will also hold. In Table 2, we compare the enthalpies and Gibbs energies computed from the corrected global minimum conformer with the composite derived from explicit computation of all isomers.

The data in Table 2 show that there is uniformity across the three model chemistries. The mean absolute deviations are, on average, less than 1 kJ/mol with standard deviations that are nearly as large. The latter often result from the presence of one very large deviation in the group. Half of the enthalpies show a difference between methods of more than 1 kJ/mol with most of these occurring in the *trans* compounds. For the Gibbs energies, only the *cis*-propyl- and pentyldiazenes show a difference of more than 1 kJ/mol and this difference occurs in all three model chemistries. These differences between corrected thermodynamic properties and those in which all conformers were explicitly computed are consistent with those reported in refs 14 and 15.

SCHEME 2: Reactions for the Assessment of Group Additivity Values



SCHEME 3: Reactions for the Assessment of Isomerization Energies



Group Equivalents and Resolution of Conflicts between Experimental and Computational Measurements. In Scheme 2, we show three reactions whose thermochemistry we have examined with an eye toward the examination of methylene group equivalents. Each reaction is given as a pair; the first for the diazenes, and the second for the corresponding alkenes. Thus, the first (eq 3) asks the question: what is the change in enthalpy when a methylene is inserted adjacent to the double bond? Is it the same for nitrogen−nitrogen and carbon−carbon double bonds and are they similar to the Benson methylene equivalent? In each pair of reactions, there is an implied second set because we will examine this question for both the *cis* and *trans* compounds. The second (eq 4) probes the effect of inserting a methylene between the first and second atoms out from the double bond and the third (eq 5) examines the effect of adding a methylene two atoms and beyond from the double bond. In Table 3, we summarize our first set of results.[41]

For reaction 3, there is a significant difference between adding the first methylene group to *trans*-diazene and *cis*-diazene. Insertion of a methylene into *trans*-diazene brings the total system energy ~25 kJ/mol lower. Subsequent homologues have an energy change slightly lower than this averaging −23.4 ± 0.5 kJ/mol. The energy change is nearly constant as the substitution on the opposite carbon progresses from monosubstituted to disubstituted to trisubstituted. The corresponding changes for the *trans*-alkenes average −30.8 ± 1.3 kJ/mol. Hence insertion of a methylene into an alkene is more exothermic than into the comparable diazene.

The first methylene inserted into *cis*-diazene itself brings the total system energy nearly 31 kJ/mol lower. More energy is released inserting a methylene into *cis*-diazene than into *trans*-diazene. As was pointed out earlier, *cis*-diazene is 22.1 kJ/mol less stable than the *trans* form. This is a much larger difference than is observed for the alkenes and can be rationalized on two grounds: (1) the nitrogen−nitrogen bond in the diazenes (~126 pm) is shorter than that of the alkenes (134 pm) and gives rise to increased repulsion between the substituents, and (2) there are two lone pairs in the diazenes, which in the case of the *cis* isomers will be repulsive. Although methyl is bulkier than hydrogen, the energy difference between the two methyl diazenes is only 17.0 kJ/mol. It could be argued that the carbon−carbon bond being longer may provide less steric repulsion than hydrogen, however, we believe that relief of the repulsion of the electron pairs may also make a significant contribution to this. In Figure 2, we show the HOMO for both *cis*-diazene and *cis*-methyl diazene. In the latter, the delocalization of the lone pair onto the methyl group allows for relief of the repulsions of the two adjacent lone pairs. A similar argument has been proposed for preference of the *cis*-dihalodiazenes over those of the *trans* isomers.[42]

Turning to the remainder of the *cis*-diazenes entries for reaction three, we note that the overall average for the series is 0.3 ± 10.7 kJ/mol. Most methylene insertions move the energy about 2.5 kJ/mol lower suggesting that the energy released by the addition of a methylene unit is nearly canceled by the increased steric repulsion encountered when hydrogen is replaced by a methyl group. Bonding a secondary substituent to the nitrogen atom changes the methylene insertion process to endothermic by about the same magnitude as for a primary substituent. Placing a tertiary carbon at the nitrogen results in an increase of just over 20 kJ/mol in energy and methylene insertion into a diazene with a *cis tert*-butyl group is nearly 45 kJ/mol more endothermic than the corresponding *trans* compounds. Moving the secondary or tertiary carbon one atom away from the nitrogen has about the same energy effect as those having no branching. For the alkenes, we find that the *cis* isomer is close to five kJ/mol less stable than the *trans* isomers regardless of substitution patterns except when a tertiary carbon is adjacent to the double bond. In these cases, the *cis* isomer is ~20 kJ/mol less stable than the *trans*.

Reaction 4 is the insertion of a methylene one carbon away from the nitrogen−nitrogen double bond. For the diazenes, the energy effect is nearly the same for both the *cis* and *trans* isomers and is more exothermic than the first methylene insertion. It is also more exothermic than the corresponding insertion into an alkene. Indeed, the average for the alkenes, *cis* or *trans*, is very close to the Benson value. In reaction 5, all four groups, *cis*- and *trans*-diazenes and *cis*- and *trans*-alkenes show that once you are two carbons removed from the double bond, the effects of the double bond vanish. Hence, from this point onward, insertion of a methylene group into either class of compounds can be estimated by the Benson methods.

Given that there are significant differences between the thermochemistry of the diazenes and alkenes, we decided to examine the effect of isomerizing the side chain, both adjacent to and away from the double bond. In Scheme 3, reactions 6 and 7 isomerize a secondary carbon to a tertiary adjacent to the double bond and away, respectively. Reaction eight is the

TABLE 3: Group Equivalents[a] (G3MP2) for Reactions 3 through 5

	diazenes		alkenes	
	trans	*cis*	*trans*	*cis*
		Reaction 3		
		R		
H	−25.3	−30.3	−28.6	
methyl	−22.7	−1.0	−30.1	−25.1
ethyl	−23.0	−2.8	−31.6	−26.4
propyl	−23.1	−3.2	−30.6	−26.5
butyl	−23.1	−1.1	−30.7	−25.7
pentyl	−23.1	−1.0	−30.7	−25.8
hexyl	−23.1	−3.0	−30.7	−25.8
heptyl	−23.1	−3.0	−30.7	−25.8
octyl	−23.1	−3.0		
isopropyl	−23.3	2.8	−30.1	−24.8
sec-butyl	−23.6	1.9	−27.2	−22.1
sec-pentyl	−23.7	1.6	−32.1	−27.1
sec-hexyl	−23.8	1.5	−32.7	−27.7
isobutyl	−23.2	−5.2	−31.5	−27.5
isopentyl	−23.1	−2.9	−32.1	−27.1
isohexyl	−23.2	−3.1	−32.3	−27.4
tert-butyl	−23.3	20.9	−30.4	−10.2
tert-pentyl	−23.6	20.0	−30.8	−10.4
tert-hexyl	−23.7	19.9	−31.3	−11.0
neopentyl	−23.6	−4.1	−31.2	−27.9
av	−23.4	0.3	−30.8	−23.8
std dev	0.5	10.7	1.3	5.9
		Reaction 4		
		R		
H	−26.2	−26.6	−18.7	−18.7
methyl	−26.5	−28.5	−20.1	−19.9
ethyl	−26.8	−28.5	−19.6	−18.8
propyl	−26.7	−28.5	−19.7	−18.2
butyl	−26.7	−28.5	−21.6	−21.4
pentyl	−26.7	−28.6	−22.2	−22.0
hexyl	−26.7	−28.6	−22.8	−22.6
isopropyl	−26.9	−28.7	−21.0	−20.9
isobutyl	−26.8	−28.6	−20.5	−20.3
isopentyl	−26.7	−28.6	−20.3	−20.3
isohexyl	−26.8	−28.6	−20.3	−20.2
tert-butyl	−27.3	−28.9	−20.7	−21.4
neopentyl	−26.3	−28.0	−20.6	−20.4
av	−26.7	−28.4	−20.6	−20.4
std dev	0.3	0.5	1.1	1.3
		Reaction 5		
		R, R′ = H		
methyl	−20.0	−20.1	−22.0	
ethyl	−20.6	−22.6	−20.1	
propyl	−20.8	−20.9	−19.4	
butyl	−20.7	−18.7	−18.8	
pentyl	−20.7	−20.7	−18.2	
hexyl	−20.7	−20.7	−17.6	
isopropyl	−19.7	−19.0	−17.4	
isobutyl	−21.0	−21.1	−19.7	
R, R′ = CH_3				
methyl	−20.1	−20.5	−21.1	−19.9
ethyl	−20.6	−20.5	−20.1	−22.1
propyl	−20.8	−20.8	−19.5	−19.9
butyl	−20.7	−20.7	−18.8	−20.7
pentyl	−20.7	−20.7	−18.2	−20.7
hexyl	−20.7	−20.7	0.0	0.0
isopropyl	−19.5	−16.8	−21.8	−22.1
isobutyl	−21.0	−21.3	−21.8	−22.1
av	−20.5	−20.2	−20.2	−21.1
std dev	0.4	1.3	1.2	0.9

[a] kJ/mol.

TABLE 4: Group Equivalents (G3MP2)[a] for Reactions 6 and 7

	diazenes		alkenes	
	trans	*cis*	*trans*	*cis*
		Reaction 6		
		R, R′ = H		
methyl	−15.1	−15.3	−7.6	
ethyl	−15.6	−15.1	−8.5	
propyl	−15.6	−15.0	−5.6	
butyl	−15.8	−17.3	−5.8	
av	−15.5	−15.7	−6.9	
std dev	0.2	0.9	1.2	
		R, R′ = CH_3		
methyl	−15.3	−9.3	−7.1	−6.0
ethyl	−16.1	−12.2	−5.1	−4.9
propyl	−16.2	−12.3	−7.6	−7.4
butyl	−16.4	−12.7	−8.3	−8.2
av	−16.0	−11.6	−7.0	−6.7
std dev	0.4	1.4	1.2	1.3
		Reaction 7		
		n, R′ = H		
1	−7.7	−6.4	−9.2	
2	−6.6	−4.5	−6.6	
3	−6.9	−6.9	−6.9	
av	−7.0	−5.9	−7.6	
std dev	0.5	1.0	1.2	
		R, R′ = CH_3		
1	−7.8	−10.5	−10.7	−11.6
2	−6.6	−6.4	−8.7	−9.0
3	−6.9	−7.0	−9.3	−9.3
av	−7.1	−7.9	−9.6	−10.0
std dev	0.5	1.8	0.8	1.2
		Reaction 8		
		R, R′ = H		
methyl	−28.9	−23.4	−19.2	
ethyl	−26.7	−22.3	−14.6	
propyl	−26.9	−24.4	−14.7	
av	−27.5	−23.3	−16.2	
std dev	1.0	0.9	2.2	
		R, R′ = CH_3		
methyl	−29.2	−1.3	−23.9	−3.7
ethyl	−27.3	−1.2	−19.6	0.8
propyl	−27.5	−1.5	−20.8	−0.5
av	−28.0	−1.4	−21.4	−1.1
std dev	0.9	0.1	1.8	1.9

[a] kJ/mol.

isomerization of a secondary carbon to a quaternary adjacent to the double bond. For the corresponding isomerization one or more atoms removed from the double bond, we have a few examples which will be discussed, but no series. The results are shown in Table 4.

The isomerization energies for the monosubstituted diazenes have a nearly identical mean for the *cis* and *trans* isomers although the deviation for the former is larger. This mean is just over double that for the alkenes showing that increasing substitution adjacent to the double bond is more stabilizing for a diazene than for an alkene. In the case where R′ is methyl, the *trans*-diazenes show an isomerization energy comparable to that for the monosubstituted compounds. The *cis*-diazenes show a reduced energy owing to increased steric repulsions. The isomerization energies for the alkenes are comparable for both cases although the deviations are large. When the isomerization occurs away from the double bond (reaction 7), the isomerization energy drops to a level that is comparable to that of the alkenes.

Isomerization of monosubstituted double bonds to afford a quaternary carbon atom adjacent to the double bond is strongly

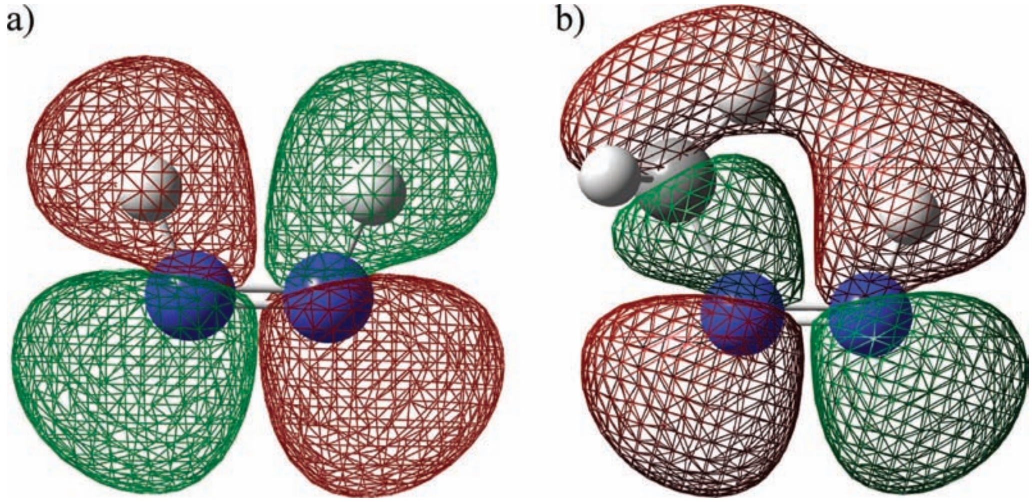


Figure 2. HOMO for (a) *cis*-diazene and (b) *cis*-methyl diazene.

TABLE 5: Enthalpies and Gibbs Energies of Formation[a] for Selected Diazenes

	literature		enthalpy			Gibbs energy		
compound	source[b]	value	G3	G3MP2	CBS-QB3	G3	G3MP2	CBS-QB3
dimethyl diazene	Rossini	148.7	156.9	157.2	156.9	245.5	245.8	245.9
methyl ethyl diazene	Rossini	120.1	129.9	130.7	130.2	246.5	247.3	247.0
methyl butyl diazene	Engel-2	78.9	89.0	90.1	89.6	263.5	264.5	264.5
diethyl diazene	Rossini	91.6	102.6	103.9	103.4	247.2	248.4	248.1
dipropyldiazene	Engel-1	51.3[c]	62.0	63.6	63.3	264.4	266.1	266.4
diisopropyldiazene	Engel-1	35.6	29.9	32.5	31.5	237.8	240.5	240.3
dibutyl diazene	Engel-2	9.2	20.7	22.6	22.2	281.1	283.0	284.1
di-*tert*-butyl diazene	Engel-1	−35.6	−41.5	−37.8	−39.5	238.7	242.5	239.9
tert-butyl (1,1,3,3-tetramethylbutyl) diazene	Engel-1	−119.3		−118.8	−119.7		292.0	289.3
3,3,5,5-tetramethylpyrazoline	Engel-1	39.3	32.7	36.8	34.0	251.7	255.9	259.4
3,4,5,6-tetrahydro-3,3,6,6-tetramethylpyridazine	Engel-1	42.0	38.0	42.4	42.0	294.0	298.4	297.0

[a] kJ/mol. [b] Rossini = ref 18; Engel-1 = ref 19; Engel-2 = ref 20. [c] The NIST Webbook (ref [13]) attributes a value of 62.4 kJ/mol for this compound to: Lebedeva, N. D.; Masalitinova, T. N.; Mon′yakova, O. N.; Oleinikova, T. P. *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 226−228.

exothermic. *trans*-Diazenes are slightly more exothermic than the *cis*, and both are more exothermic than the corresponding alkenes by 8 to 10 kJ/mol. For *trans*-disubstituted diazenes, the energy released is the same as for the monosubstituted diazenes. The corresponding alkenes show a small increase in the energy released. Both the *cis*-disubstituted diazenes and alkenes show a large drop in exothermicity with both being almost thermoneutral. Again, we see that the energy released from the isomerization is canceled by the increase in steric repulsion.

Reconciliation of Experimental and Computed Enthalpies. In Table 5, we present the computed thermodynamic properties with corrections as described above for those diazenes having an enthalpy value reported in the literature. The agreement shown in the table among the three model chemistries is quite good suggesting that the computationally more efficient G3(MP2) procedure is adequate for these compounds. Indeed, in some instances, G3(MP2) is closer than the more expensive methods.

We can begin by examining dipropyl and diisopropyl diazene. Table 5 shows a difference of 15.7 kJ/mol between the enthalpies of these two compounds. On the basis of the alkene isomerization energies from reaction 6, this is reasonable, but computation shows that isomerization should give a difference of 31.0 kJ/mol. The difference between the computational enthalpies, 32.1 kJ/mol is very close to this although we did not use these compounds to determine the average isomerization energy of diazenes in Table 4. More critical to our analysis is the difference between the dibutyl and di-*tert*-butyl diazenes as the former was used by Rossini to determine the enthalpies of the several methyl diazenes. Experiment gives a difference between the enthalpies of these compounds of 44.8 kJ/mol. Again, if we were reasoning that diazenes were like alkenes, this difference compares quite well with the value for the isomerization of two butyl groups given in Table 6 (42.8 kJ/mol). However, based on our calculations, that difference for diazenes should be 56.0 kJ/mol which is closer to the actual value of 62.2 kJ/mol. Note, that it is the di-*tert*-butyl diazene whose experimental and computational enthalpies are very close.

Rossini based his estimate for dimethyl diazene on calorimetric measurement of dibutyl diazene and methyl butyl diazene.[20] He reasoned that the enthalpy change in losing a propyl group from dibutyl diazene should be the same as the corresponding loss of from methyl butyl diazene to afford dimethyl diazene. Examination of the corresponding data in Table S3 (Supporting Information) shows this hypothesis to be correct. It is interesting that in both cases, the computed enthalpy is about ten kJ/mol higher than the experimental. Hence the computational measurements for dimethyl, methyl ethyl, and diethyl diazene vary by a comparable amount.

Is there a reason that the calorimetric measurements would be in error by this much? The presence of a mix of the *cis* and *trans* isomers is unlikely as this would cause the enthalpies to be higher than our values, not lower. The differences could be accounted for by the presence of higher molecular weight impurities, however, the experimental description of the preparation and purification of the compounds, along with the analytical methods used to assess purity leaves little room for speculation that this could be a potential problem.

Is it the computations that err? In our defense, we note that we do get some of the enthalpies within eight kJ/mol which is considered the upper limit for experimental error. In those cases where we are close, the compounds are sterically hindered and for those where we differ, they are not.

Conclusions

It is clear from Tables 3 and 4 that alkene thermochemistry is not a good basis for estimating diazene properties. The thermodynamic methylene equivalents vary from those of the alkenes, sometimes smaller than the hydrocarbon counterpart and sometimes larger. Only carbon atoms removed from the double bond can be expected to correspond to alkene thermochemistry. Even comparison of isomeric diazenes with isomeric alkenes fails when the change in substitution in adjacent to the double bond.

We have presented proposed thermodynamic properties in Table 5 for those compounds having an enthalpy value in the literature. The agreement is not always good and we have made no effort to offer a protocol which converts the computed result into a value that is close to the experiment. Although overall agreement with the literature can be poor, we note that enthalpies for several of the compounds listed in Table 5 were derived by analogy from other values, not by experimental measurement. All of the enthalpies for which the computations are within experimental error of the literature value were determined by calorimetry although the converse is not true.

Our values do include two corrections. The first is the high level correction that is inherent in the model chemistry employed and is transparent to the chemist/physicist who is performing the calculation. The second compensates for the fact that computation measures the thermodynamic properties only for the conformer being calculated while the experimental value reflects the composite energies of all conformers, proportional to their presence.

The experimental data cited in Table 5 has been used by several groups as reference data for the parametrization of their force field optimization procedures.[43,44] To the extent that computation is correct, these parameters will need to be revised.

Computational thermochemistry has long been regarded as being limited to small compounds, usually six heavy atoms. We have included in Table 5, several compounds that have eight or more heavy atoms whose enthalpies and Gibbs energies of formation have been determined with high level model chemistries including G3, G3(MP2) and CBS-QB3. Table S3 (Supporting Information) has many more. We believe that chemical systems having up to 15 first row heavy atoms are amenable to computation with the latter two of these, particularly when there is unsaturation.

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Supporting Information Available: Full citations for refs 36 and 37 and tables of enthalpies, Gibbs energies, absolute energies, and input geometries for all compounds reported here as well as those from which Tables 3 and 4 are derived. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) In the last stages of this project we obtained access to a group of SGI Altix XE310 computers which significantly accelerated the computation of the larger molecules at the high level G3 and CBS-QB3 model chemistries. As an example, we calculated 3,4,5,6-tetrahydro-3,3,6,6-tetramethylpyridazine having 10 heavy atoms. CBS-QB3 was able to finish the computation in 37 h while G3 required 153 h.

(39) The method has its limitations. We were unable to obtain an optimized structure using the CBS-QB3 method for isopropyl butyl diazene.

(40) Details of these calculations can be found in the supporting information.

(41) The data from which Tables 3 and 4 are derived is found in Table S3 of the Supporting Information.

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