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G2, G3, and complete basis set calculations of the thermodynamic properties of cis- and trans-triazene

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Abstract Following our recent study on triazane, we present a follow-up study on the thermodynamic properties of triazane's unsaturated analog, triazene. We predict optimized structural parameters, vibrational frequencies, enthalpies of formation, enthalpies of combustion, specific enthalpies of combustion, and proton affinities. Our results indicate that the cis form of triazene has a specific enthalpy of combustion of -15.2 kJ g^{-1} and the trans form has a specific enthalpy of combustion of -14.7 kJ g^{-1}.

Introduction

Research involving the search for and synthesis of new high energy (HE) materials is an ongoing quest. There are many molecules that fall into this category, and analysis of their characteristics yields several trends in structure and chemistry. These trends include strained ring structures, molecules that are unstable with respect to their combustion products, and the inclusion of various nitrogen containing functional groups, such as nitro, nitrato, and amine groups [1]. Other studies offer additional traits, such as using boron and aluminum due to the stability of their combustion products [2].

Previously, Ball [3] studied the thermodynamic properties of tetrazane, the nitrogenous analog to butane. As a follow-up study, we predicted the thermodynamic properties of triazane, the nitrogenous analog of propane; our results indicated that triazane has a specific enthalpy of combustion of about -20 kJ g^{-1} [4]. As a follow-up study to our study on triazane, we consider here the unsaturated form of triazane, triazene, as a new potential HE material, and present computational results on its structures, vibrational frequencies, and proton affinities.

Because of the double bond in triazene, triazene can exist in two conformations, the cis and trans conformations.

(1)   (2)
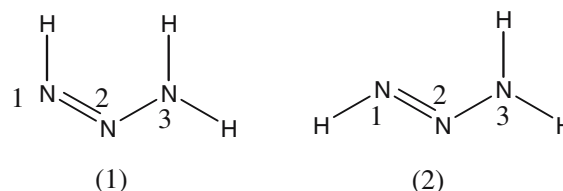
Structures 1 and 2 are the cis and trans isomers of triazene, respectively. The numbering on the nitrogen atoms will be how they are referred to in this paper. Neither conformation has been synthesized nor isolated, and computational data on either isomer is scarce.

Although triazene has never been isolated, it is the parent molecule for a whole host of organic molecules. These triazene derivatives have many applications including anticancer research [5] and organic synthesis [6]. A reaction mechanism has been proposed for the oxidation of hydrazine that creates triazene as an intermediate; this mechanism involves formation of hydrazyl radical, which dimerizes to form tetrazane, which then decomposes to form triazene and ammonia [7–11].

Magers et al. [12] studied the potential energy surface (PES) of the family of molecules having the empirical formula N_3H_3 at the SCF and MBPT(2) levels of theory using 6–31G* and DZP basis sets; they found and

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Table 1 Optimized parameters for cis-triazene (bond distances are in Å, and angles are in degrees)

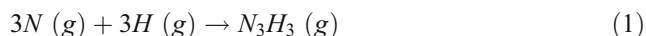| Parameter	G2, G3	CBS-QB3	CBS-APNO	[13]
r(N(1)-N(2))	1.258	1.240	1.242	1.240
r(N(2)-N(3))	1.371	1.357	1.381	
r(N(1)-H)	1.048	1.046	1.043	1.045
r(N(3)-H)	1.024	1.021	1.019	
α(H-N(3)-H)	113.8	116.4	112.6	
α(H-N(3)-N(2))	115.1	117.3	113.5	
α(N(1)-N(2)-N(3))	118.0	119.4	117.7	119.4
α(H-N(1)-N(2))	111.0	111.3	110.4	111.7
δ(H-N(1)-N(2)-N(3))	2.9	2.7	2.8	2.5
δ(N(1)-N(2)-N(3)-H)	26.5	21.0	29.2	

characterized several minimum energy geometries including that of trans-triazene. They reported the optimized structural parameters, vibrational frequencies, and infrared intensities for triazene. They did not include any results for the cis isomer of triazene.

Pu et al. [13] studied substituent effects on trans and cis isomers of diazenes having the general structure H-N=N-R, where R was H, F, OH, OCF$_3$, OCH$_3$, CN, CHO, NH$_2$, or CH$_3$. They reported the optimized parameters for both isomers of triazene, inversion barriers, and the charge on the nitrogen atoms at the B3LYP/6–311++G(d,p) level of theory.

One of the most recent studies of triazene was done by Galván et al. [14]. They compared the effectiveness of three effective Hamiltonian models, which are commonly used to model solvated systems, using triazene in water as their test case. They reported structural parameters for trans-triazene both in vacuum and in aqueous solution. They did not report optimized parameters for cis-triazene either in vacuum or in aqueous solution.

Computational details

All calculations were done on a personal computer using the Gaussian 03 [15] computational chemistry program. The calculational methods used include the G2 [16], G3 [17], and two complete basis set (CBS) methods [18]. The structures and vibrations were visualized using GaussView [19]. The infrared spectra were generated using the SWizard [20] program using a Lorentzian lineshape with a bandwidth of 15 cm^{-1} at half height. The enthalpies of formation were calculated by calculating the energies of all species in the reverse atomization reaction:

$$3N\,(g) + 3H\,(g) \rightarrow N_3H_3\,(g) \qquad (1)$$

The energy change for the reaction was corrected for the enthalpy of formation of the gaseous reactants, as obtained

Table 2 Optimized parameters for trans-triazene (bond distances are in Å, and angles are in degrees)

Parameter	G2, G3	CBS-QB3	CBS-APNO	[13]	[12]*	[14]
r(N(1)-N(2))	1.270	1.250	1.250	1.249	1.217 **1.220** *1.274*	1.271
r(N(2)-N(3))	1.358	1.348	1.368		1.348 **1.346** *1.365*	1.354
r(N(1)-H)	1.029	1.023	1.023	1.023	1.008 **1.009** *1.029*	1.035
r(N(3)-H)	1.021	1.018	1.017		1.002 **1.003** *1.021*	1.028
α(H-N(3)-H)	115.8	118.1	114.4		114.65 **115.37** *114.81*	
α(H-N(3)-N(2))	113.9	115.9	112.5		113.59 **114.16** *113.57*	113.3
α(N(1)-N(2)-N(3))	111.9	113.3	112.3	113.8	113.90 **113.93** *111.59*	112.6
α(H-N(1)-N(2))	104.4	105.4	104.9	105.9	106.82 **106.89** *103.82*	104.8
δ(H-N(1)-N(2)-N(3))	176.1	176.9	176.4	177.5	177.01 **177.25** *176.09*	159.0
δ(N(1)-N(2)-N(3)-H)	19.8	16.8	21.8		21.33 **20.77** *21.21*	16.2

* normal text denotes SCF/6–31G*, bold text denotes SCF/DZP, and italic text denotes MBPT(2)/DZP

by the NIST website [21]. Using the enthalpy of formation obtained from reaction 1, the enthalpy of combustion (ΔH$_{comb}$) can be calculated using reaction 2.

$$N_3H_3(g) + 3/4 O_2(g) \rightarrow 3/2 N_2(g) + 3/2 H_2O(\ell) \qquad (2)$$
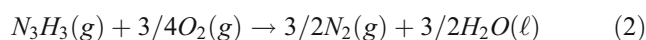
The enthalpy of formation of water, used in (2) was obtained from the NIST Webbook website [21]. Dividing the enthalpy of combustion by the molar mass gives the specific enthalpy of combustion (ΔH$_{comb,sp}$).

The proton affinity (PA) is a measure of a molecule's Lewis base strength. The proton affinity can be determined

Fig. 1 Cis-triazene. Optimized structural parameters are located in Table 1
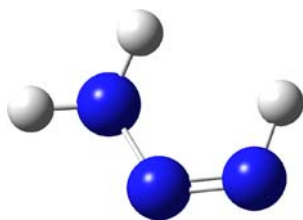
by using the enthalpy of formation determined from the enthalpy of reaction of reaction 3.

$$N_3H_3\ (g) + H^+ \rightarrow N_3H_4^+\ (g) \quad PA \equiv -\Delta H_{rxn} \quad (3)$$
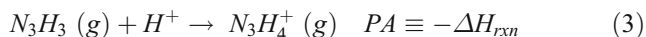
Reaction 3 assumes that a nitrogen atom is the site of protonation. Because triazene has three nitrogen atoms in three different chemical environments, the proton affinity must be calculated separately for each nitrogen atom.

Results and discussion

Optimized geometries

The optimized structural parameters for cis- and trans-triazene are located in Tables 1 and 2 respectively. The optimized geometry for cis-triazene is depicted in Fig. 1 and the optimized geometry for trans-triazene is depicted in Fig. 2. Included in each table are the previously predicted structural parameters. The numbers next to the N for the cis isomer represent the number it is labeled in structure 1, and the numbers next to the N for the trans isomer represent the number it is labeled as located in structure 2. Following the rules for functional groups in organic chemistry, in both cases nitrogen 1 is the initial nitrogen atom involved in the double bond, nitrogen 2 is the central nitrogen atom, and nitrogen 3 is the terminal nitrogen atom not involved in the double bond. For comparison, the optimized geometry for the minimum energy conformation of triazane is included in Table 3; the subscript "t" in Table 3 denotes the terminal nitrogen atoms.

Table 1 lists the optimized structural parameters for cis-triazene, and with a few exceptions the four methods are in good agreement. These exceptions are the two N-N bonds, N(1)-N(2) and N(2)-N(3); the two GX methods predict that both of these bonds are about 0.02 Å longer than the lengths predicted by the two CBS methods. As expected, both N-N bonds in cis-triazene are significantly shorter than

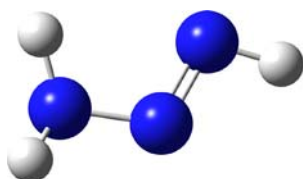**Fig. 2** Trans-triazene. Optimized structural parameters are located in Table 2

Table 3 Optimized geometric parameters for triazane (all bond lengths are in Å, and all angles in degrees)

Parameter	G2,G3	CBS-QB3	CBS-APNO
r (N_t-N)	1.427	1.424	1.424
r (N_t-H)	1.010	1.010	1.010
r (N-H)	1.010	1.010	1.010
α (N_tNN_t)	116.1	117.1	115.9
α (HN_tH)	106.9	107.6	106.7
α (N_tNH)	106.0	106.7	106.0
δ (N_tNN_t-H)	79.8	80.0	78.9

those observed previously in our study of triazane [4]. As Fig. 1 and the two dihedral angles suggest, cis-triazene is not planar. The NH_2 group is pyramidal as expected, and the hydrogen attached to N(1) is about 3° out of plane with the nitrogen backbone of the molecule.

The optimized structural parameters for trans-triazene are located in Table 2. As with the cis isomer, the four methods predict slightly different values for the two N-N bonds. The two GX methods predict a double bond distance of 1.270 Å, which is 0.02 Å greater than the distance predicted by the two CBS methods. Analogous to the cis isomer, the trans isomer is also non-planar, with dihedral angles of about 176.5° and 19.5° for the H-N(1)-N(2)-N(3) and N(1)-N(2)-N(3)-H dihedral angles, respectively.

Vibrations and vibrational spectra

Table 4 lists the vibrational frequencies for cis-triazene and Table 5 lists the vibrational frequencies for trans-triazene. Both spectra are plotted in Fig. 3 to the same scale. Both

Table 4 Vibrational frequencies, infrared intensities, and approximate mode descriptions for cis-triazene (vibrational frequencies in cm^{-1}, and infrared intensities in km mol^{-1})

G2, G3	CBS-QB3	CBS-APNO	Description
440.4 (20.6)	513.5 (17.4)	448.7 (17.4)	NH_2 twist
681.2 (24.6)	627.4 (8.3)	627.8 (84.6)	NH_2 wag
749.6 (294.0)	489.1 (257.0)	713.9 (203.7)	NH_2 rock
1094.8 (97.6)	971.2 (53.2)	1087.8 (87.5)	N(1)H rock
1186.6 (47.3)	1067.8 (55.1)	1177.9 (47.8)	N(3)-N(2) stretch
1394.1 (4.7)	1236.9 (6.6)	1377.6 (6.0)	sym N-H wag
1636.8 (141.0)	1453.8 (120.5)	1614.0 (135.5)	N(1)H wag
1831.9 (62.9)	1616.4 (139.3)	1802.5 (67.2)	NH_2 bend
1910.9 (77.5)	1652.4 (15.8)	1896.4 (85.2)	N(1)-N(2) stretch
3473.1 (35.1)	3087.5 (80.0)	3457.4 (28.7)	N(1)-H stretch
3715.4 (8.0)	3414.5 (4.3)	3703.1 (7.4)	sym N(3)-H stretch
3883.7 (30.6)	3648.7 (32.5)	3871.8 (33.5)	asym N(3)-H stretch

Table 5 Vibrational frequencies, infrared intensities, and approximate mode descriptions for trans-triazene (vibrational frequencies in cm^{-1}, and infrared intensities in km mol^{-1})

G2, G3	CBS-QB3	CBS-APNO	Description
517.8 (76.6)	596.2 (73.0)	518.8 (78.6)	NH$_2$ twist
685.7 (7.2)	649.7 (32.3)	686.1 (5.2)	NH$_2$ wag
760.7 (403.8)	467.1 (241.8)	722.8 (347.3)	NH$_2$ rock
1068.2 (50.1)	943.1 (51.0)	1064.3 (48.0)	N(1)H rock
1210.9 (58.5)	1119.3 (85.8)	1203.5 (72.9)	N(3)-N(2) stretch
1413.5 (46.0)	1247.5 (47.1)	1396.9 (48.7)	sym N-H wag
1643.2 (7.3)	1487.7 (10.0)	1626.3 (4.3)	N(1)-H wag
1816.9 (53.9)	1624.7 (23.0)	1789.5 (60.1)	NH$_2$ bend
1889.0 (86.9)	1597.2 (128.7)	1875.9 (97.8)	N(1)-N(2) stretch
3685.3 (0.5)	3404.8 (0.3)	3678.9 (2.4)	N(1)-H stretch
3744.6 (11.7)	3456.4 (1.6)	3729.5 (9.6)	sym N(3)-H stretch
3899.3 (30.3)	3675.6 (40.7)	3887.8 (34.8)	asym N(3)-H stretch

molecules exhibit C$_1$ symmetry and their vibrations transform as:

$$\Gamma(triazene) = 12A \quad in\ C_1$$

Because the A symmetry species is infrared-active, both the cis and trans isomers will have 12 infrared active vibrations. The data in Tables 4 and 5 show that all four

calculational methods predict 12 vibrations with non-zero intensities.

Table 4 shows good agreement among the vibrational frequencies calculated by the two GX methods and those calculated by the CBS-APNO method. The CBS-QB3 method predicts vibrational frequencies lower than the other three methods, sometimes almost 400 cm^{-1} lower as seen for the N(1)-H stretch (3473.1 cm^{-1}, 3087.5 cm^{-1}, and 3457.4 cm^{-1} for the GX, CBS-QB3, and CBS-APNO respectively). All three methods are fairly consistent in predicting approximately the same infrared intensities. One other point of interest in Table 4 is that the CBS-QB3 method predicts the NH$_2$ rock (489.1 cm^{-1}) to have the lowest vibrational frequency, where as the GX and CBS-APNO methods both predict the NH$_2$ twist (440.4 cm^{-1} and 448.7 cm^{-1} respectively) to have the lowest vibrational frequency.

The data in Table 5 shows similar patterns to those in Table 4. Again the GX and CBS-APNO methods demonstrate a high level of agreement among vibrational frequencies, whereas the CBS-QB3 method predicts lower vibrational frequencies than both the GX and CBS-APNO methods. Similar to Table 4, the CBS-QB3 method predicts the NH$_2$ rock (467.1 cm^{-1}) to have the lowest vibrational frequency; the GX and CBS-APNO methods both predict the NH$_2$ twist (517.8 cm^{-1} and 518.8 cm^{-1} respectively) to have the lowest vibrational frequency. All three methods still predict fairly similar infrared intensities.

Previous infrared vibrational data is available for the trans isomer of triazene only. Magers et al. [12] reported vibrational frequencies, infrared intensities and approximate descriptions. The vibrational frequencies calculated by
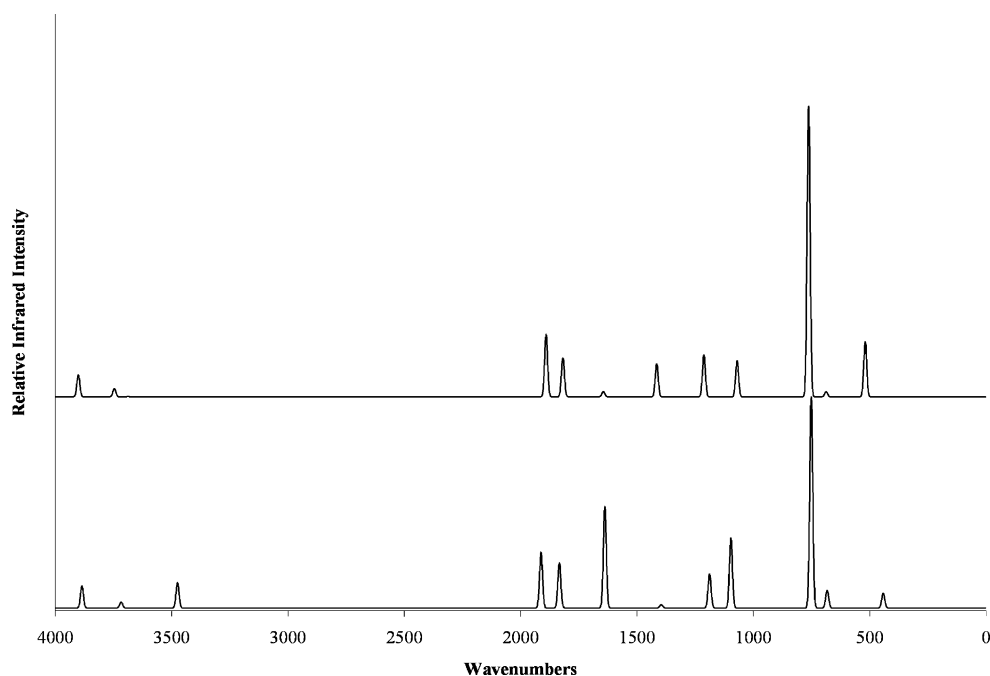

Fig. 3 Infrared spectra for cis and trans isomers of triazene. Wavenumbers are in cm^{-1} and relative infrared intensities are graphed to the same scale

Table 6 Thermodynamic properties of cis- and trans-triazene (all values in kJ mol^{-1}, except specific enthalpies of combustion, which are in kJ g^{-1})

ΔH_f	G2	G3	CBS-QB3	CBS-APNO
cis	251.0	258.7	251.1	255.1
trans	228.9	236.3	228.7	232.6
ΔH_{comb}				
cis	−679.8	−687.4	−679.8	−683.8
trans	−657.6	−665.0	−657.4	−661.3
$\Delta H_{comb,sp}$				
cis	−15.1	−15.3	−15.1	−15.2
trans	−14.6	−14.8	−14.6	−14.7

Fig. 4 Protonated structures of cis-triazene. See Tables 8 and 9 for optimized structural parameters

Magers et al.'s [12] SCF method using the 6–31G* basis set and the vibrational frequencies calculated by the SCF method using the DZP basis-set are in good agreement with each other and correspond well with the vibrational frequencies predicted by both the GX and CBS-APNO methods. Magers et al.'s [12] MBPT(2) method predicts vibrational frequencies between those predicted by the CBS-QB3 method and those predicted by the GX and CBS-APNO methods. Magers et al. [12] list infrared intensities for both the SCF/DZP and MBPT(2) calculations; these infrared intensities are consistent between the two methods and are similar to those calculated by our four methods. Magers et al.'s [12] mode descriptions correspond identically for both of their SCF calculations, but their MBPT(2) calculation predicts a switch of the relative energy of the N(1)-N(2) stretch and the NH$_2$ stretch. Magers et al.'s [12] mode descriptions follow the same relative order as those predicted by our CBS-QB3 method with the exception of their MBPT(2) calculation.

Figure 3 shows both spectra have peaks at approximately the same wavelengths, but these peaks have distinctly different infrared intensity values. Based on the intensity of the peaks it may be possible to tell the two isomers apart should they ever be synthesized. However, because of the similarity in the frequencies of the vibrations, careful isotopic studies may be needed to confirm the identity of the conformations.

Table 7 Proton affinities for cis- and trans-triazene, in kJ mol^{-1}

	G2	G3	CBS-QB3	CBS-APNO
cis-triazene				
N(1)	880.9	884.3	880.3	885.6
N(2)	792.9	794.6	793.3	795.3
trans-triazene				
N(1)	858.8	861.9	858.0	863.1
N(2)	778.3	779.7	778.6	781.1
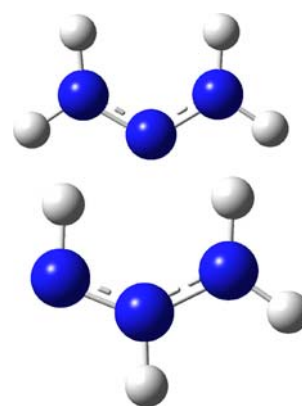
Energies of reaction

Table 6 lists the enthalpies of formation (ΔH_f) and combustion (ΔH_{comb}) along with the specific enthalpy of combustion ($\Delta H_{comb,sp}$) for each isomer of triazene. The cis isomer of triazene is predicted to have a slightly higher enthalpy of formation at about 254 kJ mol^{-1} compared to about 232 kJ mol^{-1} for the trans isomer of triazene. This is to be expected due to steric hindrance in the cis isomer. While mapping the PES in our previous study on triazane [4] we observed that when the nitrogen atoms' lone pairs are in the eclipsed conformation at its maximum energy. Similarly in cis-triazene, the lone pairs are located in close proximity and this leads to repulsion, causing cis-triazene to have a higher energy than trans-triazene, which does not have the lone-pairs located in such close proximity. Our study on triazane [4] predicted its most stable conformer to have an enthalpy of formation of about 199 kJ mol^{-1}, which is about 30 kJ mol^{-1} lower in energy then the more stable trans isomer. Ball's study on tetrazane predicted an enthalpy of formation of about 293 kJ mol^{-1} [3]; this is about 40 kJ mol^{-1} higher than the enthalpy of formation of cis-triazene. For further comparison, cis-2-butene has an enthalpy of formation of −7.7 kJ mol^{-1} and trans-2-butene has an enthalpy of formation of −10.8 kJ mol^{-1} [21].
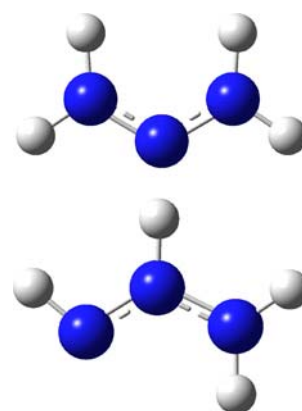

Fig. 5 Protonated minimum energy geometries of trans-triazene. See Tables 8 and 10 for optimized structural parameters

Table 8 Optimized structural parameters of protonated triazene at nitrogen 1. (all bond distances are in Å and all angles in °)

Parameter	G2,G3	CBS-QB3	CBS-APNO
r (N-H)	1.025	1.023	1.020
r (N-N)	1.277	1.269	1.272
α (H-N-H)	120.0	119.7	120.4
α (H-N-N)	124.7	124.6	124.1
α (N-N-N)	118.5	119.5	118.5
δ (H-N-N-N)	0.0	0.0	0.0

The specific enthalpies of combustion are also shown in Table 6. Comparing triazene to triazane, shows that the specific enthalpies of combustion for both isomers are about 5 kJ g^{-1} less negative than those of triazane (~ -20 kJ g^{-1}) [4]. Using the enthalpy of formation for RDX of 192 kJ mol^{-1} [21], one can calculate the specific enthalpy of combustion for RDX; the specific enthalpy of combustion using this enthalpy of formation is -7.4 kJ g^{-1}. This means the trans isomer of triazene gives off about twice as much energy as RDX on a per-gram basis. Comparing the specific enthalpies of combustion to those of our previous studies shows that the specific enthalpy of combustion of both isomers is considerably less negative than most of the boron-containing molecules we previously studied [22–25], which we predicted to have specific enthalpies of combustion up to 165 kJ g^{-1}. The usefulness of triazene as an HE material will depend on its density and velocity of detonation, both of which can be determined if it is synthesized.

Table 7 lists the proton affinities for both isomers of triazene. For the proton affinities we assumed that one of the nitrogen atoms was the site of protonation. This means that for each isomer of triazene there are three possible protonation sites. Protonation at the first and second nitrogen atoms produce a mostly planar structure that has electron delocalization running the entire length of the nitrogen backbone. Protonation at the third nitrogen causes the

Table 9 Optimized structural parameters of protonated cis-triazene at nitrogen 2. (all bond lengths in Å, and all angles in °)

| Parameter	G2, G3	CBS-QB3	CBS-APNO
r (H-N(1))	1.033	1.030	1.031
r (N(1)-N(2))	1.264	1.237	1.239
r (N(2)-H)	1.031	1.029	1.027
r (N(2)-N(3))	1.312	1.326	1.344
r (N(3)-H)	1.018	1.014	1.015
α (H-N-H)	121.7	121.2	116.8
α (H-N(3)-N(2))	119.6	119.0	113.7
α (N(3)-N(2)-H)	114.6	113.8	114.3
α (N(3)-N(2)-N(1))	131.3	130.9	129.9
α (N(2)-N(1)-H)	110.3	111.5	110.3
δ (H-N(1)-N(2)-N(3))	0.0	2.0	5.1

Table 10 Optimized structural parameters for protonated trans-triazene at nitrogen 2. (all bond lengths in Å, and all angles in °)

| Parameter	G2, G3	CBS-QB3	CBS-APNO
r (N(1)-H)	1.028	1.025	1.026
r (N(1)-N(2))	1.266	1.238	1.241
r (N(2)-H)	1.035	1.033	1.030
r (N(2)-N(3))	1.305	1.318	1.335
r (N(3)-H)	1.015	1.012	1.014
α (H-N-H)	123.1	122.4	118.2
α (H-N(3)-N(2))	119.2	118.1	114.4
α (N(3)-N(2)-H)	114.3	113.6	114.0
α (N(3)-N(2)-N(1))	121.8	122.6	122.0
α (N(2)-N(1)-H)	108.2	109.8	109.0
δ (H-N(1)-N(2)-N(3))	178.2	177.2	174.1

triazene to undergo a decomposition reaction that ultimately forms an ammonium ion and diatomic nitrogen. The protonated structures are depicted in Figs. 4 and 5; in both figures the top structure is the result of protonation at nitrogen 1 and the bottom structure is the result of protonation at nitrogen 2. The optimized structural parameters for these molecules are located in Tables 8, 9, and 10. Table 8 gives the optimized geometry for the nitrogen 1 protonated form for both isomers.

The proton affinities of the two nitrogen atoms that did undergo protonation successfully show that the two nitrogen atoms have considerably different chemical environments. For both isomers N(1) is considerably more basic than N(2); N(1) in the cis isomer has a proton affinity greater than N(2) by about 90 kJ mol^{-1} and nitrogen 1 in the trans isomer has a proton affinity greater than nitrogen 2 by about 80 kJ mol^{-1}. The difference in proton affinities seems reversed at first; one would expect the central nitrogen atom to be more basic due to the fact that it has two nitrogen atoms next to it, both of which can be used to balance out the positive charge taken on by accepting a proton. As our calculations show, this is not the case. Protonation at nitrogen 1 on either isomer creates a structure that looks like structure 3.

Structure 3 makes it explicit that the double bond that originally existed between nitrogen atoms 1 and 2 has lowered by half a bond order and the bond between nitrogen atoms 2 and 3 has raised by half a bond order. Computing formal charges shows that nitrogen atoms one and three bear a charge of $+0.5$ each. This is compared to protonation at N(2) which produces a structure similar to

(3)
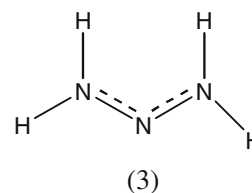
that of structure 4 for the cis isomer and a structure similar to that of structure 5 for the trans isomer.

(4)   (5)
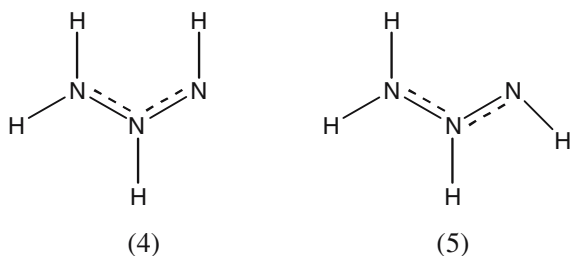
Computation of formal charges on structures five and six yield a −0.5 charge on N(1), a +0.5 charge on N(3) and a +1 charge on N(2). The conclusion is protonation at N(1) leads to a better distribution of charge than protonation at N(2).

Comparing the proton affinities of triazene to those of triazane show that N(1) of the cis isomer is roughly equal in base strength to the central nitrogen in triazane's conformation 3 (about 880 kJ mol^{-1}), where protonation at N(1) in the trans isomer is roughly equal in base strength to the central nitrogen atom of triazane's conformation 1 (about 863 kJ mol^{-1}) [4]. For further comparison, the proton affinity of nitrogen one in trans-triazene is similar to that of ammonia, 851.4 kJ mol^{-1} [26]. This suggests that triazene will behave strongly as a base.

Conclusions

In this study, we have predicted the optimized structure, vibrational frequencies, infrared intensities, enthalpies of formation, enthalpies of combustion, specific enthalpies of combustion, and proton affinities of cis- and trans-triazene. Our optimized structures agree well with the previously calculated data. Our infrared spectra suggest that should both isomers of triazene be synthesized, it may be possible to tell the two isomers apart based on the predicted infrared spectra, though detailed isotopic studies may be needed to confirm the conformations. Our specific enthalpy of combustion results predict that cis- and trans-triazene give off about twice as much energy per gram as RDX, making triazene a good candidate for a new HE material; however, triazene does not give off as much energy as triazane or the boron compounds we have studied in the past. The usefulness of triazene as a HE material will depend on its density and velocity of detonation, both of which can be determined if it is synthesized.

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