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Predicting Solid-State Heats of Formation of Newly Synthesized Polynitrogen Materials by Using Quantum Mechanical Calculations

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We present density functional theory level predictions and analysis of the basic properties of newly synthesized high-nitrogen compounds together with 3,6-bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine (BTT) and 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAAT), for which experimental data are available. The newly synthesized high-nitrogen compounds are based on tricycle fused 1,2,4-triazine and 1,2,4,5-tetrazine heterocycles. In this work, the molecules BTT and DAAT have been studied in order to validate the theoretical approach and to facilitate further progress developments for the molecules of interest. Molecular structural properties are clarified, and IR spectra predictions are provided to help detection of those compounds in the experiment. The energy content of the molecules in the gas phase is evaluated by calculating standard enthalpies of formation, by using a special selection of isodesmic reaction paths. We also include estimates of the condensed-phase heats of formation and heats of sublimation in the framework of the Politzer approach. The obtained properties are consistent with those new high-nitrogen compounds being a promising set of advanced energetic materials.

1. Introduction

In both modern civil and military applications, there is a clear need for energetic materials that have superior performance and lower vulnerability to undesired stimuli, that is, higher insensitivity to thermal shock, friction, and electric discharge. These properties are essential to improve the personnel safety and to reduce the warhead vulnerability problems. A key challenge along that direction is the tendency for performance and insensitivity characteristics to be mutually exclusive,[1] with improved insensitivity bringing inferior performance (as, e.g., for TATB) and vice versa, especially within the realm of traditional energetic compounds. One promising approach to overcoming that challenge is to explore new energetic compounds with increased nitrogen content, which is the direction pursued by many recent research and development efforts, as reviewed in refs 1−4. The characteristic feature of such high-nitrogen compounds is that, in contrast to traditional energetic molecules, their energy content comes primarily from the high heats of formation due to the large number of energetic N−N and C−N, rather than from the overall heat of combustion (oxidation of carbon backbone). The high-nitrogen compounds also tend to have an additional benefit of being less toxic for the user and the environment, because higher portion of their decomposition products is dinitrogen. An important class of high-nitrogen molecules is heterocyclic compounds,[2,3] which have received much recent attention in an energetic materials role because of a very advantageous combination of thermal stability, heat of formation, and density, as well as oxygen balance. Efforts to synthesize this class of novel energetic materials have been made on pyrazoles,[5] pyrazines and pyridines,[6,7] tetrazines,[8,9] furazans,[10,11] and tetrazoles.[12] Most recently, in an effort to improve performance and stability of functionalized heterocycles, a new class of such compounds, tricyclic fused 1,2,4-triazines, has recently been synthesized.[13] The tricyclic structure is expected to help stability via electron delocalization and distribution of energetic functions. However, so far, there is no experimental data on densities and heats of formation for this new class of energetic compounds, in particular, heats of formation in condensed phase, which is one of the important parameters for the evaluation of energetic materials performance. To facilitate further progress in the characterization and development of 1,2,4-fused-triazines-based heterocycles together with 3,6-bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine (BTT) and 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAAT), here, we report on quantum-mechanics-based theoretical analysis of structural, vibrational, and energetic properties of those newly synthesized molecules.

2. Computational Details

All calculations on structural property of these molecules were performed in the framework of density functional theory (DFT) at the levels of B3LYP/6-311+G(3df,2p), BLYP/6-311+G(3df,2p), B3PW91/6-311+G(3df,2p), and PBEPBE/6-311+G(3df,2p) by using G03 quantum chemistry package.[14] About the accuracy for the prediction of various properties of energetic molecules, there are some review papers available in the literatures.[15] Because we also focus on energies of isodesmic reactions for heats of formation in these molecules, the B3LYP/6-311+G(3df,2p) calculation has been used as our results on heats of formation in comparison with experiments. It is known that most B3LYP level calculations with appropriate basis sets are able to reproduce experimental values on isodesmic reactions better than others, such as other DFT level and Hartree−Fock level with a medium-sized basis sets. However, other DFT level calculations were also carried out for the purpose of comparison.

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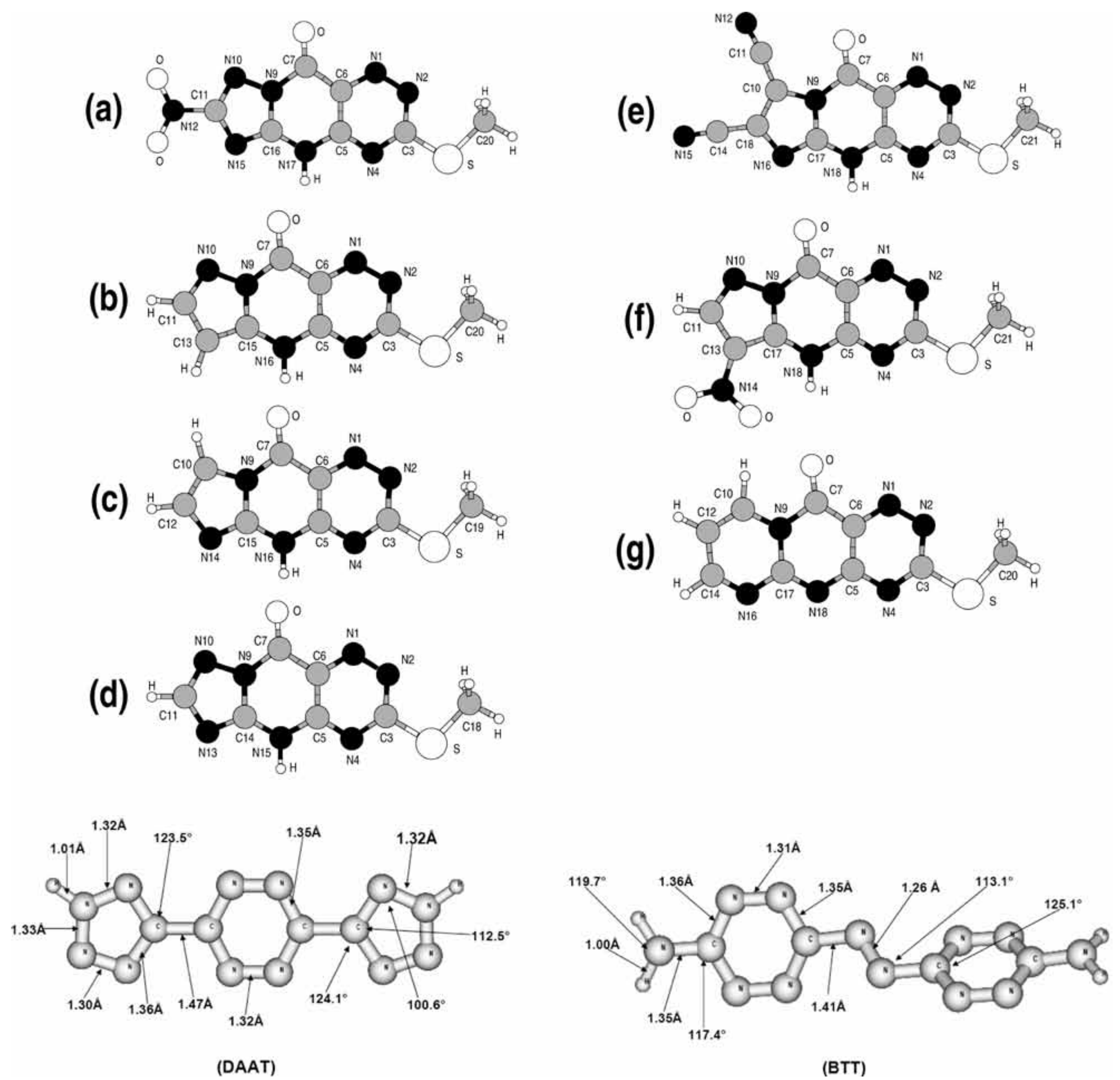


Figure 1. Optimized structure and atomic site labeling. The structures in panels a−g correspond to molecules 3a and 3c−h of Table 1 of ref 5. DAAT and BTT are 3,3′.-azobis(6-amino-1,2,4,5-tetrazine) and 3,6-Bis(2H-tetrazol-5-yl)-1,2,4,5-tetrazine compounds with optimized structural parameters, respectively.

Harmonic vibrational frequencies were calculated at the same theory level as that used to fully optimize molecular structures, which enables us to confirm the real minima. A hybrid representation (numerical and analytical) Gaussian basis DFT implementation was used for calculations on electronic density and electrostatic potential in numerical grids with optimized geometric structures of these molecules. Post processing of the electrostatic potential and valence electron density for Politzer fitting requires presentation of the data on a real-space mesh. A tetrahedral technique is then used to calculate the area of the iso-surface for a given charge density or electrostatic value.[16] The structures were optimized until the total residual force was within maximum force 0.00045 au/Å and root mean square 0.003 au/Å. Seven different cases of fused 1,2,4-triazines presented in the Product column of Table 1 of ref 13 as 3a, 3c−h as well as reference molecules such as BTT and DAAT were studied. The initial molecular structures of the newly synthesized polynitrogen molecules were constructed to match schematic structures/bond arrangements given in the cited table of ref 13.

3. Results and Discussions

The optimized molecular structures are presented in Figure 1. Outside of two hydrogen atoms of the sulfur-attached methyl group in each structure, all the structures were found to be planar, with only slight, less than 0.002°, deviations for structures (a) and (e) in Figure 1. Tables 1−7 summarize the optimized bond lengths and bond angles for each structure at the levels of B3LYP/6-311+G(3df,2p), by following atom labeling of Figure 1. The overall behavior of bond lengths and angles is similar to those in other triazine-fused system (see, e.g., ref 17). The N−N, C−N, and C−C bond lengths follow natural tendencies in that the bonds that are expected to be of double-bond type (e.g., according to the diagrams in ref 13)

TABLE 1: Selected Structural Information for Molecule in Figure 1a

Bond Lengths			
N1−N2	1.31	C7−N9	1.44
N1−C6	1.34	N9−N10	1.35
N2−C3	1.36	N9−C16	1.37
C3−N4	1.34	N10−C11	1.31
N4−C5	1.32	C11−N12	1.46
C5−C6	1.42	C11−N15	1.36
C5−N17	1.37	N15−C16	1.31
C6−C7	1.48	C16−N17	1.36
Bond Angles			
N2−N1−C6	120.0	C7−N9−N10	124.5
N1−N2−C3	118.1	C7−N9−C16	126.5
N2−C3−N4	126.3	N10−N9−C16	109.0
C3−N4−C5	114.6	N9−N10−C11	100.9
N4−C5−C6	121.4	N10−C11−N12	120.5
N4−C5−N17	118.3	N10−C11−N15	118.2
C6−C5−N17	120.3	N12−C11−N15	121.2
N1−C6−C5	119.6	N9−C16−N15	111.4
N1−C6−C7	117.5	N9−C16−N17	120.2
C5−C6−C7	123.0	N15−C16−N17	128.4
C6−C7−N9	109.8	C5−N17−C16	120.2

TABLE 2: Selected Structural Information for Molecule in Figure 1b

Bond Lengths			
N1−N2	1.31	C7−N9	1.42
N1−C6	1.33	N9−N10	1.36
N2−C3	1.35	N9−C15	1.38
C3−N4	1.33	N10−C11	1.32
N4−C5	1.33	C11−C13	1.42
C5−C6	1.42	C13−C15	1.37
C5−N16	1.36	C15−N16	1.38
C6−C7	1.49		
Bond Angles			
N2−N1−C6	120.0	C7−N9−N10	122.3
N1−N2−C3	117.9	C7−N9−C15	126.1
N2−C3−N4	126.7	N10−N9−C15	111.6
C3−N4−C5	114.4	N9−N10−C11	104.2
N4−C5−C6	121.3	N10−C11−C13	113.5
N4−C5−N16	118.7	C11−C13−C15	103.3
C6−C5−N16	120.0	N9−C15−C13	107.4
N1−C6−C5	119.7	N9−C15−N16	119.4
N1−C6−C7	117.9	C13−C15−N16	133.2
C5−C6−C7	122.3	C5−N16−C15	121.2
C6−C7−N9	111.0		

TABLE 3: Selected Structural Information for Molecule in Figure 1c

Bond Lengths			
N1−N2	1.31	C7−N9	1.41
N1−C6	1.33	N9−C10	1.39
N2−C3	1.36	N9−C15	1.38
C3−N4	1.33	C10−C12	1.36
N4−C5	1.33	C12−N14	1.39
C5−C6	1.42	N14−C15	1.30
C5−N16	1.36	C15−N16	1.38
C6−C7	1.48		
Bond Angles			
N2−N1−C6	120.0	C7−N9−C10	128.1
N1−N2−C3	117.8	C7−N9−C15	126.3
N2−C3−N4	126.8	C10−N9−C15	105.6
C3−N4−C5	114.6	N9−C10−C12	105.1
N4−C5−C6	121.0	C10−C12−N14	111.9
N4−C5−N16	118.8	C12−N14−C15	103.9
C6−C5−N16	120.2	N9−C15−N14	113.5
N1−C6−C5	119.9	N9−C15−N16	119.1
N1−C6−C7	118.1	N14−C15−N16	127.4
C5−C6−C7	122.0	C5−N16−C15	121.1
C6−C7−N9	111.2		

TABLE 4: Selected Structural Information for Molecule in Figure 1d

Bond Lengths			
N1−N2	1.31	C7−N9	1.42
N1−C6	1.33	N9−N10	1.36
N2−C3	1.36	N9−C14	1.37
C3−N4	1.33	N10−C11	1.32
N4−C5	1.33	C11−N13	1.37
C5−C6	1.42	N13−C14	1.31
C5−N15	1.36	C14−N15	1.37
C6−C7	1.49		
Bond Angles			
N2−N1−C6	120.0	C7−N9−N10	124.8
N1−N2−C3	118.0	C7−N9−C14	126.6
N2−C3−C4	126.5	N10−N9−C14	108.6
C3−N4−C5	114.5	N9−N10−C11	101.9
N4−C5−C6	121.3	N10−C11−N13	116.7
N4−C5−N15	118.5	C11−N13−C14	101.3
C6−C5−N15	120.1	N9−C14−N13	111.6
N1−C6−C5	119.6	N9−C14−N15	120.1
N1−C6−C7	117.7	N13−C14−N15	128.3
C5−C6−C7	122.7	C5−N15−C14	120.4
C6−C7−N9	110.1		

are shorter than those of the single-bond type. The N−N and C−N bond lengths cover ranges of 1.30−1.37 Å and 1.30−1.39 Å, respectively, with an exception of C−N bonds attaching the C=O fragments [bonds C7−N9 Figure 1a−g] and the nitro group [bonds C11−N12 in Figure 1a and C13−N14 in Figure 1f], which are around 1.42−1.44 Å. We also performed harmonic vibrational spectra calculations, which confirmed the studied structures as being total-energy local minima (as indicated by the absence of imaginary frequencies). Based on the calculated vibrational properties, the infrared absorption spectra were evaluated, and the results are presented in Figure 2. The IR intensity peaks are in good overall agreement with the available experimentally measured IR frequencies in ref 13 [see Figure 2a], when assuming that some of the experimental peaks correspond to double peaks in theoretical data (e.g., peaks near 1500 cm^{-1}). A more reliable matching of theoretical and experimental IR peaks would be needed to measure the relative-intensity data (not reported).

To determine the energy content of the energetic compounds studied, we have calculated their standard heats of formation. The gas-phase standard heat of formation ΔH^{f}_{gas} can be evaluated on the basis of Hess's Law, by considering a real or hypothetical reaction that would produce the desired molecule out of a set of other molecules, the gas-phase standard heats of formation of which are already known. In particular, the unknown heat of formation can be obtained as a sum of the reaction energy (computed theoretically) and the correspondingly weighted sum of the standard heats of formation (measured) of the relevant reactants. Unless an expensive high-level method is used, the accuracy of the final result for ΔH^{f}_{gas} depends appreciably on the choice of the reaction. To limit such inaccuracies (via error compensation), it is important to only consider reactions that retain the number and type of bonds, the so-called bond separation isodesmic reactions,[18] which were shown to yield accurate thermochemical results already at the DFT level of treatment of energetic reactions.[19] To further improve accuracy for ring-containing molecules, it is also desirable to use an additional guideline of ring conservation.[20] On the basis of such considerations, within the constraints of availability of measured reference data, for the best accuracy of ΔH^{f}_{gas} predictions, we

TABLE 5: Selected Structural Information for Molecule in Figure 1e

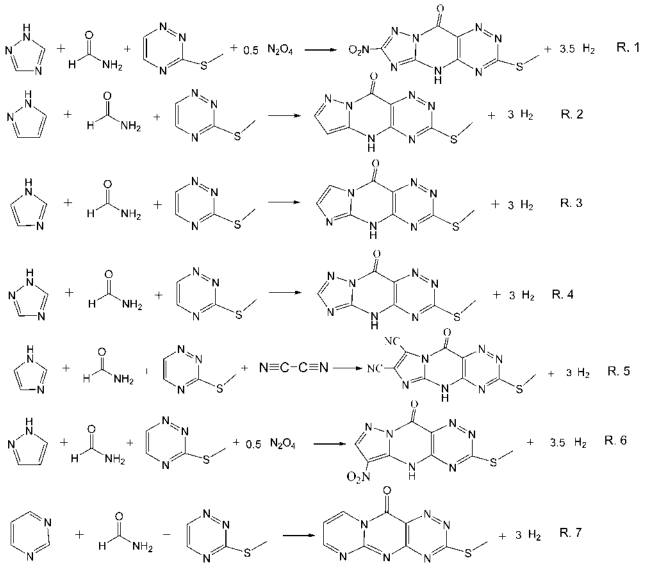
Bond Lengths			
N1−N2	1.30	N9−C10	1.39
N1−C6	1.33	N9−C17	1.37
N2−C3	1.35	C10−C11	1.41
C3−N4	1.33	C10−C13	1.38
N4−C5	1.32	C11−N12	1.16
C5−C6	1.41	C13−C14	1.42
C5−N18	1.36	C13−N16	1.37
C6−C7	1.47	C14−N15	1.16
C7−N9	1.43	N16−C17	1.30
Bond Angles			
N2−N1−C6	119.9	C10−N9−C17	105.5
N1−N2−C3	118.1	N9−C10−C11	125.6
N2−C3−N4	126.4	N9−C10−C13	104.6
C3−N4−C5	114.6	C11−C10−C13	129.8
N4−C5−C6	121.3	C10−C13−C14	126.4
N4−C5−N18	118.6	C10−C13−N16	111.8
C6−C5−N18	120.1	C14−C13−N16	121.8
N1−C6−C5	119.8	C13−N16−C17	104.0
N1−C6−C7	117.8	N9−C17−N16	114.0
C5−C6−C7	122.5	N9−C17−N18	119.6
C6−C7−N9	110.9	N16−C17−N18	126.4
C7−N9−C10	128.6	C5−N18−C17	121.1
C7−N9−C17	125.8		

TABLE 6: Selected Structural Information for Molecule in Figure 1f

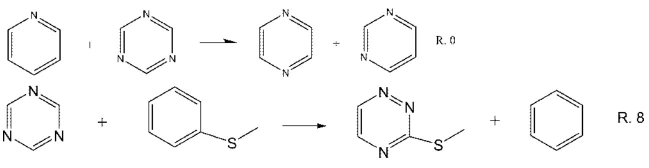
Bond Lengths			
N1−N2	1.31	C7−N9	1.43
N1−C6	1.34	N9−N10	1.37
N2−C3	1.36	N9−C17	1.36
C3−N4	1.34	N10−C11	1.31
N4−C5	1.32	C11−C13	1.42
C5−C6	1.42	C13−N14	1.41
C5−N18	1.36	C13−C17	1.39
C6−C7	1.48	C17−N18	1.36
Bond Angles			
N2−N1−C6	119.9	C7−N9−C17	125.1
N1−N2−C3	118.1	N10−N9−C17	112.3
N2−C3−N4	126.4	N9−N10−C11	105.0
C3−N4−C5	114.4	N10−C11−C13	111.8
N4−C5−C6	121.5	C11−C13−N14	130.0
N4−C5−N18	118.7	C11−C13−C17	105.1
C6−C5−N18	119.8	N14−C13−C17	125.0
N1−C6−C5	119.6	N9−C17−C13	105.9
N1−C6−C7	117.6	N9−C17−N18	121.6
C5−C6−C7	122.8	C13−C17−N18	132.5
C6−C7−N9	110.6	C5−N18−C17	120.1
C7−N9−N10	122.6		

devise the following set of hypothetical isodesmic (or nearly isodesmic) reactions for molecules in reactions from R.1 to R.7, respectively

In these isodesmic reactions, 1,2,4-triazole, formamide, dinitrogen tetroxide, pyrazole, imidazole, cyanogens, 1,3-diazine, and dihydrogen molecules together with 1,2,4-trazine, 3-methylthio molecules are taken as reference molecules, the experimental heats of formation of which are available except for 1,2,4-triazine, 3-methlythio. To compute heats of formation of this compound, we have derived another isodesmic reaction R.8, where 1,3,5-triazine and benzene,(methylthio) molecules serve as reactants. In this isodesmic reaction, benzene and 1,2,4-triazine,(methylthio) will be produced as products. Thus, in this isodesmic reaction, 1,3,5-triazine, benzene,(methylthio), and benzene serve as reference molecules. Finally, these reference molecules all have available experimental heats of formation, given in Table 8.



First, to verify calculations on isodesmic reaction energies, we designed an isodesmic reaction R.0 which deals with pyridine, 1,3,5-triazine, 1,3-diazine, pyrazine, and 1,3-diazine heterocyclic aromatic organic compounds, because experimental heats of formation are available. With this isodesmic reaction, we have computed the enthalpy of 1,3,5-triazine molecule. The theoretical value is 54.81 kcal mol^{-1} in comparison with an experimental value of 53.98 kcal mol^{-1} at B3LYP/6-31G(d) level, indicating good agreement with experiments.



In this work, we have recognized that most experimental data on structures, vibrational spectra, and heats of formation for these newly synthesized fused 1,2,4-triazine heterocycles are so limited. Thus, we have considered two 1,2,4,5-tetrazine heterocycles, BTT and DAAT, because experimental data on these two compounds are available. In addition, to validate and facilitate further progress in the characterization and development of 1,2,4-fused-triazines-based heterocycles, DAAT and BTT, high-nitrogen 1,2,4,5-tetrazine derivatives, are all well-referenced energetic compounds. The optimized structural properties of DAAT and BTT compounds are given in Figure 1. To compute enthalpies of BTT and DAAT, we also have designed four isodesmic reactions R.9−R.12, and the reactions R.11−R.12 are designed to compute enthalpies of 1H-1,2,3,5-tetrazol and 1,2,4,5-tetrazine molecules, for which experimental enthalpies in gas phase are not available. In these isodesmic reactions, methane, ammonia, 1H-1,2,4-triazole, 1,3,5-trazine, 1,2,4-triazine, and 1,3-diazine are taken as reference compounds or molecules, which are also listed in Table 8.

With these isodesmic reactions and reference compounds such as 1,2,4-triazole, formamide, dinitrogen tetroxide, 1H-pyrazole, 1H-imidazole, cyanogens, 1,3-diazine, dihydrogen, and 1,2,4-trazine, 3-methylthio molecule, we computed enthalpies of these molecules in gas phases. The enthalpies in condensed phases were estimated by using Politzer approach.[16,32−34] All results on heats of formation are listed in the Tables 9−10. The heats of formation in gas phase for the seven molecules together with

TABLE 7: Selected Structural Information for Molecule in Figure 1g

Bond Lengths			
N1−N2	1.30	C7−N9	1.46
N1−C6	1.34	N9−C10	1.37
N2−C3	1.37	N9−C17	1.41
C3−N4	1.32	C10−C12	1.36
N4−C5	1.34	C12−C14	1.42
C5−C6	1.42	C14−N16	1.30
C5−N18	1.35	N16−C17	1.36
C6−C7	1.45	C17−N18	1.31
Bond Angles			
N2−N1−C6	119.1	C7−N9−C10	116.5
N1−N2−C3	117.6	C7−N9−C17	122.6
N2−C3−N4	127.3	C10−N9−C17	120.9
C3−N4−C5	115.5	N9−C10−C12	120.1
N4−C5−C6	118.4	C10−C12−C14	116.7
N4−C5−N18	117.8	C12−C14−N16	124.2
C6−C5−N18	123.8	C14−N16−C17	119.4
N1−C6−C5	122.1	N9−C17−N16	118.6
N1−C6−C7	117.3	N9−C17−N18	123.2
C5−C6−C7	120.6	N16−C17−N18	118.1
C6−C7−N9	111.7	C5−N18−C17	118.1

TABLE 8: Reference Data (Experimental) Used in Standard Heats of Formation Evaluation

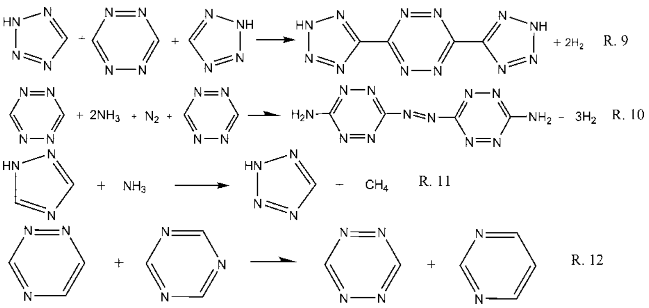
name	formula	ΔH^{f}_{gas} (kcal/mol)	source ref
1H-1,2,4-triazole	$C_2H_3N_3$	46.1	21
1H-pyrazole	$C_3H_4N_2$	42.9	22
1H-imidazole	$C_3H_4N_2$	33.3	22
cyanogen	C_2N_2	73.87	24
formamide	CH_3NO	−44.5	26
ammonia	H_3N	−10.97	25
methane	CH_4	−17.89	24
benzene	C6H6	19.8	30
dinitrogen tetroxide	N_2O_4	2.17	24
benzene,(methylthio)	C_7H_8S	23.25	23
pyridine	C_5H_5N	33.50	31
1,3-diazine	$C_4H_4N_2$	46.8	28
1,3,5-triazine	$C_3H_3N_3$	53.98	29
pyrazine	$C_4H_4N_2$	46.86	27

TABLE 9: Calculated Values of Politzer Descriptors *A*, *ν*, *σ* and Heats of Sublimation[a]

molecule	*A* (bohr^2)	$\sigma_{tot}{}^2$	ν	ΔH_{sub} (kcal/mol)
(a)	1061	2.01×10^{-3}	0.226	44.5
(b)	959	2.99×10^{-3}	0.237	40.5
(c)	959	1.95×10^{-3}	0.236	37.3
(d)	940	2.28×10^{-3}	0.244	37.4
(e)	1148	2.12×10^{-3}	0.231	51.9
(f)	1058	1.58×10^{-3}	0.246	43.4
(g)	999	1.86×10^{-3}	0.232	39.7
DAAT	960	3.12×10^{-3}	0.216	40.7
BTT	881	3.46×10^{-3}	0.178	34.4

[a] Labels a−g refer to molecule structures shown in Figure 1a−g, respectively.

BTT and DAAT are listed in the ΔH^{f}_{gas} column of Table 10, obtained by using PBE, BLYP, B3LYP, and B3PW91 functionals.



For judging the potential of the studied compounds in the energetic-material role, it is also important to know their standard heats of formation in the condensed phase, ΔH^{f}_{cond}. Given the lack of crystal structure information and additional complexities/costs of direct condensed-phase calculations in this case, here, we will only provide the best empirical estimates ΔH^{f}_{cond} that do not demand the full direct crystal-phase simulations. In particular, by assuming that intramolecular interactions in the phases of interest should be mainly noncovalent (such as van der Waals interactions, as in another case of fuzed triazines[17]), to estimate ΔH^{f}_{cond}, we employ the empirical Politzer approach,[32−34] which has been successfully applied to many other energetic compounds.[35,36] The Politzer approach links thermodynamic properties of energetic materials in condensed phases to the electronic properties of the corresponding energetic molecules in the gas phase, such as certain features of the distribution of the electrostatic potential on the molecular surface. In particular, we can evaluate the condensed-phase heat of sublimation ΔH_{sub} by using the following empirical expression:[32]

$$\Delta H_{sub} = \beta_1 A^2 + \beta_2(\nu\sigma_{tot}^2)^{0.5} + \beta_3 \qquad (9)$$

Here, A is the molecular surface area, ν quantifies the degree of balance between positive and negative potential on the molecular surface, σ^2_{tot} describes the variability of the electrostatic potential, and β_{1-3} are correlation coefficients determined via fitting to empirical data. In the present work, we calculate electrostatic-potential distribution and the resulting Politzer descriptors A, ν, σ^2_{tot} by using the same computational techniques as that previously described in ref 16 in the framework of numerical pseudopotential atomic orbital basis method.[37] For the current estimates, we use the same values of β_{1-3} coefficients as those published in ref 16, $\beta_1 = 3.56 \times 10^{-5}$, $\beta_2 = 618.15$, and $\beta_3 = -8.70$. Although the previous fit was based on CHNO compounds (without sulfur), our analysis indicates that the vicinity of the sulfur atom does not contain any noticeable contribution to the polarization of the electrostatic-potential distribution. The computed Politzer descriptor values in the level of B3LYP/6-311+G(3df,2p) are listed in Table 9 together with ΔH_{sub}, and the resulting predictions for ΔH^{f}_{cond} (evaluated as $\Delta H^{f}_{cond} = \Delta H^{f}_{gas} - \Delta H_{sub}$) are given in Table 10 at the same-level calculations. We see that the seven molecules studied indeed have very high positive heats of formation, which are comparable to, for example, CL-20 (98 kcal/mol) and various other high-nitrogen compounds discussed in refs 1−4. The trends within the given set of molecules are similar between the gas-phase and condensed-phase results, with the highest heat of formation reached by molecule (e), presumably because of the presence of additional C−N bonds from the two cyano group attachments. When comparing the calculations with other functionals on heats of sublimation for these compounds, we found that the calculations with B3LYP and B3PW91 give almost the same results, with less than 1.0 kcal mol^{-1} difference. The same observation was also shown for heats of formation in the gas phase, although there is an exception for the DAAT compound, for which the difference is about 3.86 kcal mol^{-1}. From our calculations on heats of formation in the gas phase, the maximum difference is about 23.24 kcal mol^{-1}. It appeared also on DAAT compound between PBE and B3PW91 calculations. In comparison with experimental data on DAAT and BTT compounds, B3LYP calculations on these energetic compounds give better agreement.

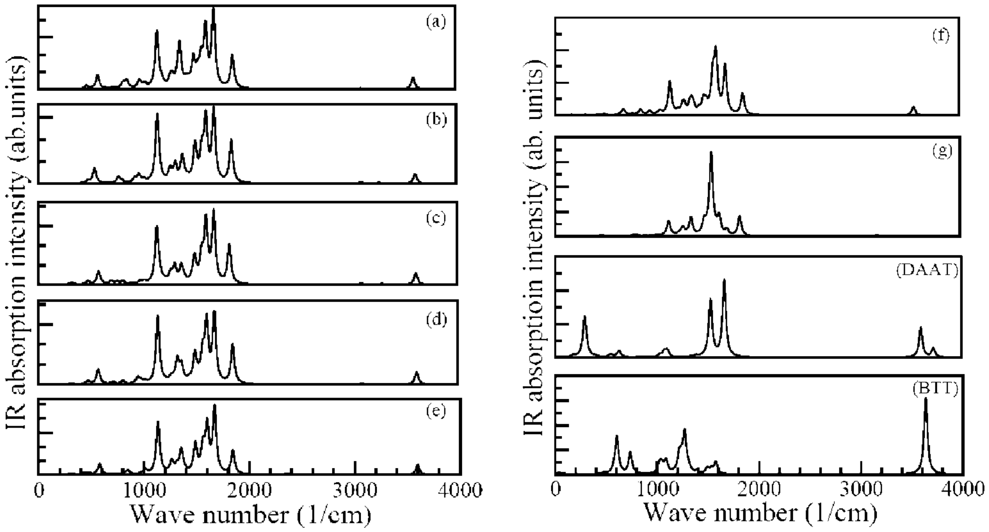
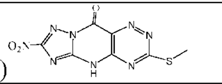
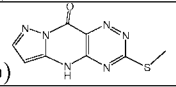
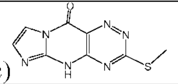
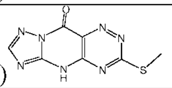
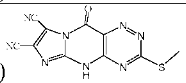
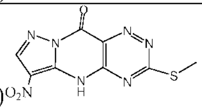
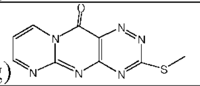
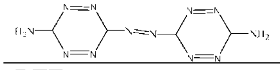
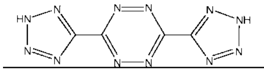


Figure 2. Theoretically calculated IR absorption intensity versus vibrational frequency (wavenumber). Panels a−g correspond to the different molecular structures a−g in Figure 1, respectively. The calculated frequencies are adjusted by a factor of 0.89 fitted to reproduce the highest-frequency mode. The vertical marks in panel a show the experimentally measured IR frequencies for the corresponding structure, as reported in ref 5.

TABLE 10: Theoretical Enthalpies in kcal mol^{-1}

Molecules	PBE	BLYP	B3LYP	B3PW91	B3LYP	B3LYP
Properties	ΔH^f_{gas}				ΔH_{sub}	ΔH^f_{cond}
 (a)	92.36	95.90	99.21	98.10	44.5	54.71
 (b)	82.50	84.72	91.51	90.61	40.5	51.01
 (c)	66.31	68.78	75.08	74.04	37.3	37.78
 (d)	83.85	86.20	92.66	91.66	37.4	55.26
 (e)	138.19	141.71	148.76	147.73	51.9	96.86
 (f)	80.35	83.33	86.50	86.09	43.4	43.10
 (g)	88.95	91.70	100.07	98.92	39.7	60.37
DAAT 	224.86	236.84	248.10	244.24	40.7	207.4 (206.0)[a]
BTT 	240.47	242.73	254.68	255.14	34.4	220.28 (223.7)[b]

[a] Experimental data.[38] [b] Experimental data.[39]

4. Summary

In summary, by using first-principles calculations at the DFT level, we have studied the basic properties of the newly synthesized fused 1,2,4-triazine, DAAT- and BTT-based energetic compounds. In particular, we characterize the molecular structures and vibrational properties, providing IR spectra predictions that can be used to help proper identification of those molecules in experiment. Based on specially designed sets of isodesmic reactions, standard gas-phase heats of formation are predicted. We also provide estimates of the condensed-phase heats of formation, in the framework of the Politzer model. From those results, we find that the high-nitrogen compounds, with their high-energy content, are a very promising set of potential advanced energetic materials. Finally, as we can see through the various results given in this paper, the B3LYP/6-311+G(3df,2p) level calculations may give better enthalpies than the other level calculations, in comparison with experimental data on BTT and DAAT compounds.

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