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The Gaussian G4 enthalpy of formation of propargylamine and propargyloxy derivatives of triazido-*s*-triazine

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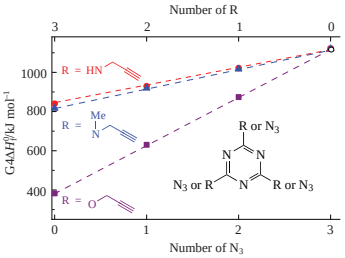
Enthalpies of formation in gas phase of three series of energetic derivatives of triazido-*s*-triazine containing propynyloxy, propynylamine and methylpropynylamine groups were calculated using G4 method. Contributions of each group to the enthalpy of formation of the discussed compounds were estimated in order to apply the increment method for quick estimation of this thermodynamic parameter for substituted *s*-triazines.



Keywords: G4-enthalpy of formation, triazido-*s*-triazine, *s*-triazine derivatives, group-contribution to the enthalpy.

Compounds based on 1,3,5-triazine (*s*-triazine), containing 51.8% of nitrogen and being of high chemical and thermal stability, can be considered as components of different energy condensed systems (ECSs).[1,2] One of the first energetic compounds based on *s*-triazine was 2,4,6-triazido-1,3,5-triazine **1**. It was proposed by US Army Armaments Research, Development & Engineering Center in 2009 as the first eco-friendly azide.[3] However, its application is strictly limited due to the extremely low stability to external exposure. Therefore, investigation of propynyloxy and propynylamine derivatives of **1** with higher stability is of great interest. The first ones include 2,4-diazido-6-(prop-2-yn-1-yloxy)-1,3,5-triazine **2a**,[4] 2-azido-4,6-bis(prop-2-yn-1-yloxy)-1,3,5-triazine **2b**[5] and 2,4,6-tris-(prop-2-yn-1-yloxy)-1,3,5-triazine **2c**.[6] Among propynylamine derivatives of **1**, there are 4,6-diazido-*N*-(prop-2-yn-1-yl)-1,3,5-triazine-2-amine **3a**, 6-azido-N^2,N^4-bis(prop-2-yn-1-yl)-1,3,5-triazine-2,4-diamine **3b**,[7] N^2,N^4,N^6-tri(prop-2-yn-1-yl)-1,3,5-triazine-2,4,6-triamine **3c**,[8] also their *N*-methyl derivatives such as 4,6-diazido-*N*-methyl-*N*-(prop-2-yn-1-yl)-1,3,5-triazine-2-amine **4a**, 6-azido-N^2,N^4-dimethyl-N^2,N^4-di(prop-2-yn-1-yl)-1,3,5-triazine-2,4-diamine **4b**[6] and N^2,N^4,N^6-trimethyl-N^2,N^4,N^6-tri(prop-2-yn-1-yl)-1,3,5-triazine-2,4,6-triamine **4c**. Structural formulae of these compounds are given in Figure 1.

It can be assumed that compounds **2**–**4c** can act as a more stable alternative for 1,4-diethynylbenzene that tend to sublimation. Utilizing of the latter as solid fuel dispersants can increase by 22% the flight range of an aircraft with a ramjet engine in comparison with propellants based on the other high-enthalpy polynitrogen compounds.[9] On the contrary, hyperbranched poly(triazine-triazole)s based on **2a**,**b**, **3a**,**b** and **4a**,**b**, which are the AB_2† type monomers, can act as promising modifiers of physicomechanical and technological characteristics of energetic polymer binders.[11] It should be noted there is a lack of experimental data on the enthalpy of formation of most

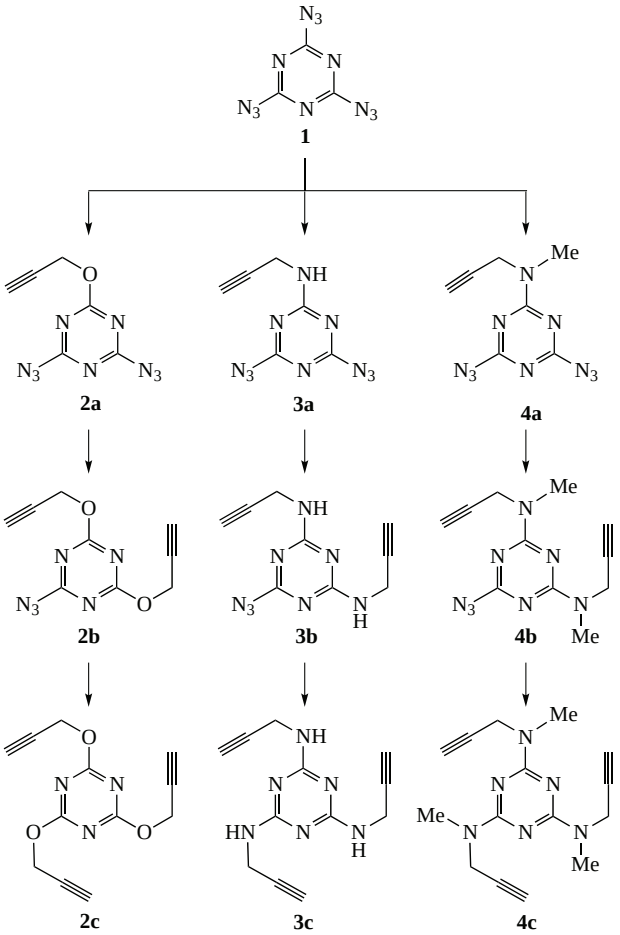


Figure 1 Structures of *s*-triazine **1** and its propynyloxy/propynylamine derivatives.

† AB_2 type monomers[10] are compounds that contain reactive groups of two types. The polyaddition of AB_2 type monomer is carried out exclusively as a result of the reactions of groups A with B, while the interaction of group A with A and group B with B should not occur.

Table 1 ΔH_f^0 values for derivatives of *s*-triazine (gaseous phase).

Propynyloxy derivatives	ΔH_f^0/kJ mol^{-1} (kJ kg^{-1})	Propynylamine derivatives	ΔH_f^0/kJ mol^{-1} (kJ kg^{-1})	Methylpropynylamine derivatives	ΔH_f^0/kJ mol^{-1} (kJ kg^{-1})
2a	874.1 (4028)	**3a**	1022.3 (4733)	**4a**	1016.4 (4419)
2b	630.3 (2740)	**3b**	929.6 (4077)	**4b**	919.2 (3591)
2c	382.3 (1573)	**3c**	840.2 (3501)	**4c**	816.2 (2890)

mentioned derivatives of compound **1**. Assessing the energy characteristics of these compounds using group contribution method is impossible due to the absence of the theoretical and experimental data on contribution of functional groups and *s*-triazine core to their enthalpy of formation. As result, the potential of these compounds as energy condensed system cannot be estimated.

In order to demonstrate the promise of **2**–**4c**, and AB_2 type monomers as ECS components or modifiers, as well as to predict their thermodynamic characteristics, the theoretical investigations are necessary. It is appropriate to use quantum chemistry approaches, among others, Gaussian-n type (Gn) composite methods to determine the gas-phase enthalpy of formation (ΔH_f^0). The latest version of these methods, Gaussian-4 (G4) theory, reaches an overall accuracy of 3.3 kJ mol^{-1} for a test set of 270 experimental values of enthalpy of formation.[12]

All the calculations were performed using the Gaussian 09 software package. The geometry optimization and conformational analysis of the compounds under study were carried out by the density functional theory (DFT) method in the M06-2X/6-311++G(d,p)[13–15] approximation. The optimized geometry of the most stable conformers was used to calculate their energy parameters by the G4 method (see Online Supplementary Materials). The ΔH_f^0 values were calculated based on atomization reaction.[16,17] All calculations were performed for the gas phase.

It is known[18,19] that ΔH_f^0 value of gas-phased **1** calculated using the G4 method is 1120.8 kJ mol^{-1}, while for condensed phase ΔH_f^0 is of 1053 kJ mol^{-1}. The difference in ΔH_f^0 correlates well with the experimental enthalpy of sublimation (83.3 ± 3.3).[20] At the same time, ΔH_f^0 for gas-phased *s*-triazine was calculated to be 223.1 kJ mol^{-1}, while experimental value in gas phase according to US National Institute of Standards and Technology[21] is of 224.7 ± 4.6 kJ mol^{-1}. Thus, the enthalpy of formation of the compounds can be calculated quite precisely using selected theoretical method.

The further calculations showed that the ΔH_f^0 for gas-phased **3c** is 840.2 kJ mol^{-1}, while for **2c** this value barely reached 382.3 kJ mol^{-1} (Table 1). Insignificant difference in ΔH_f^0 of **3c** and 1,4-diethynylbenzene (ΔH_f^0 = 500.6 kJ mol^{-1} = = 3973 kJ kg^{-1})[22] reveals **3c** as an effective dispersant due to its potentially greater thermal stability. In case of **2c**, its rather low enthalpy of formation makes it unable for spontaneous combustion.

As expected, AB_2 type monomers such as propynylamine-containing derivatives of **1** possess significantly higher enthalpy of formation than that of propynyloxy-containing counterparts. As can be seen, ΔH_f^0 shows a slight decrease when replacing amine hydrogen atom in **3b** or **3c** by a methyl group (see Table 1).

It would appear that AB_2 type monomers containing mutual reactive azide and ethynyl groups are failed to fulfill the requirements for fuel components. However, their melting points (and hence the polymerization temperature of propynylamine derivatives of **1**[7]) is close to the onset of destruction temperature of azide groups. Thus, it can be assumed that monomers **3b** and **3c** can be useful as dispersants.

On the other hand, polyaddition of AB_2 type monomers results in hyperbranched triazine-triazole polymers, which possess just ~230 kJ mol^{-1} lower enthalpy of formation compared to that of starting monomers due to the value of the polyaddition exo-effect.[23] This make them potentially useful as high-enthalpy modifiers of the physicomechanical characteristics of ECS.

The data given in Table 1 indicate that the ΔH_f^0 value for each type of *s*-triazine derivatives depends linearly on the content of azide group in the corresponding compounds that confirm additive contribution of each substituent. Statistical processing of the calculated thermodynamic parameters for *s*-triazine, **1**, propynyloxy and propynylamine derivatives showed that contribution of azide, propynyloxy, propynylamine, and methylpropynylamine groups to the enthalpy of formation for corresponding compounds is 298.1 ± 3.0, 53.6 ± 2.0, 203.7 ± 3.8 and 197.7 ± 2.8 kJ mol^{-1}, respectively.

The ΔH_f^0 for unsymmetric derivatives of **1** containing each one of azide, propynyloxy and propynylamine/methylpropynylamine groups [4-azido-*N*-(prop-2-yn-1-yl)-6-(prop-2-yn-1-yloxy)-1,3,5-triazine-2-amine, 4-azido-*N*-methyl-*N*-(prop-2-yn-1-yl)-6-(prop-2-in-1-yloxy)-1,3,5-triazine-2-amine] was calculated according to the additivity rule, using the contribution values. The ΔH_f^0 obtained this way (778.5 ± 8.8 and 775.5 ± 7.8 kJ mol^{-1}) correlate with those calculated by G4 method (778.8 and 772.2 kJ mol^{-1}, respectively).

In conclusion, the contribution of azide, propynyloxy, propynylamine, and methylpropynylamine groups to the enthalpy of formation of substituted *s*-triazines can be used to estimate this parameter for other promising energetic compounds containing these functional groups as well as to predict their thermodynamic characteristics and potential as energy condensed system components.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.015.

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