Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2022, **32**, 464–466

Mendeleev Communications

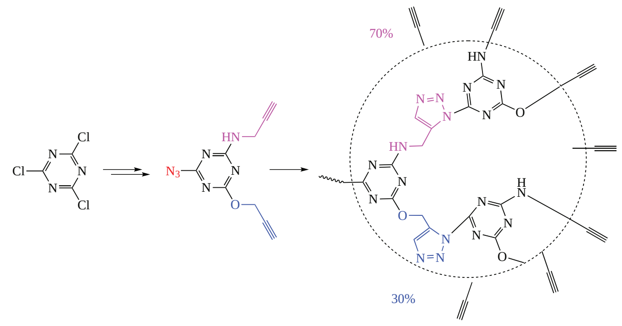
New non-symmetric azido-diacetylenic *s*-triazine monomer for polycycloaddition

Artem O. Petrov,* Sergei V. Karpov, Georgiy V. Malkov, Aleksey V. Shastin and Elmira R. Badamshina

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: petrov_ao@icp.ac.ru

DOI: 10.1016/j.mencom.2022.07.012

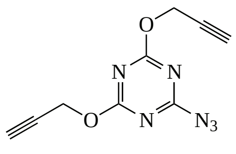
An original synthesis of a new non-symmetric energetic ABB′ type monomer, 2-azido-4-propargylamino-6-propargyloxy-*s*-triazine, with a total yield of 40% involves the sequential introduction of propargylamino, propargyloxy and azido groups into *s*-triazine. DFT investigation of azide-alkyne cycloaddition mechanism at M06-2X/6-311++G(d,p) level of theory for this monomer predicts that the regioselectivity of polycycloaddition reaction should increase with the number of propargylamino groups in the monomer structure due to the stabilization of the transition state, leading to 1,5-triazole regioisomer.



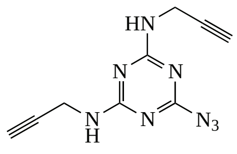
Keywords: ABB′ monomers, *s*-triazine, azides, alkynes, hyperbranched polymers, M06-2X/6-311++G(d,p), calculated Gibbs free energy, 1,2,3-triazoles.

Along with the new high-enthalpy compounds development,[1] one of dynamic directions in energy condensed systems is the modification of existing compositions.[2] Application of various branched polymers as modifiers for energetic materials (EM) is heavily investigated.[2–6] The most promising compounds in terms of their properties are hyperbranched polymers (HBPs) which can be obtained effortlessly by AB$_n$ ($n \geqslant 2$) monomer polyaddition.[7–10] In particular, energetic azido-acetylenic monomers,[11,12] the polycycloaddition products of which contain a significant amount of 1,2,3-triazoles, can be used for that purpose. *s*-Triazine is suitable as a core for AB$_2$ monomers[11] since its derivatives are often considered as promising EM constituents.[13,14]

We previously obtained azido-diacetylenic monomers of AB$_2$ type, namely, 2-azido-4,6-bis(propargyloxy)-*s*-triazine (ABPOT)[12] and 6-azido-4,6-bis(propargylamino)-*s*-triazine (ABPAT).[15] Gas-phase enthalpy of formation of ABPOT calculated using Gaussian-4 (G4) theory equals 630.3 kJ mol^{-1}, and that value for ABPAT is 929.6 kJ mol^{-1}.[16] Despite the heat of azide-alkyne polycycloaddition (AAC) reaching 230–270 kJ mol^{-1},[16–18] ABPOT- and ABPAT-based triazine-triazole HBPs are highly promising for applications as high-enthalpy EM modifiers. However, ABPOT exhibits low resistance to spontaneous polymerization due to a low melting point (41 °C), while this value for ABPAT is essentially higher (151 °C), close to the onset temperature of thermal destruction. That fact limits the possibility of obtaining ABPAT-based HBP in bulk. It can be assumed that 2-azido-4-propargylamino-6-propargyloxy-*s*-triazine (APAPOT) (Scheme 1), an azido-diacetylenic monomer containing each of azido, propargyloxy, propargylamino groups, should possess optimal thermal characteristics, and G4 enthalpy of formation of this ABB′ monomer should be 778.8 kJ mol^{-1}.[16]



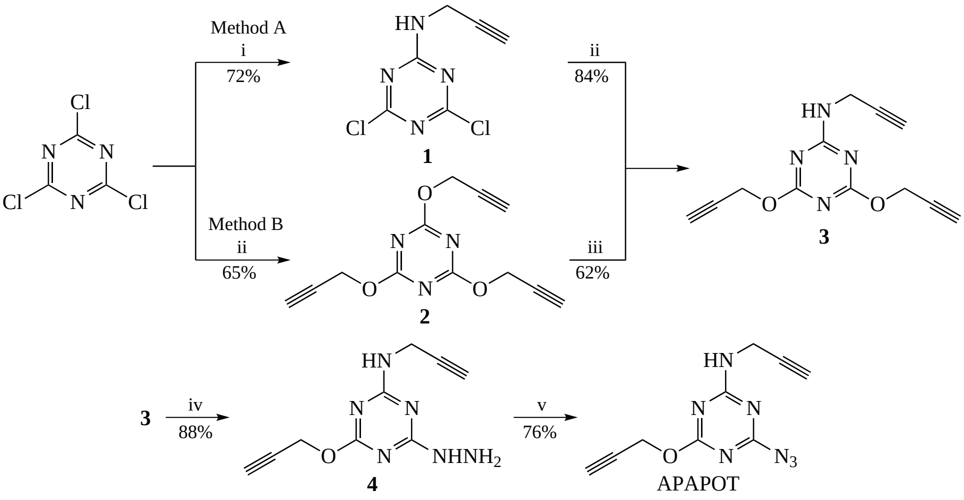
ABPOT



ABPAT

The main issue in the development of obtaining AB$_n$ monomers consists in avoiding spontaneous polymerization during the synthesis and in possibility to isolate the monomers. Therefore, the development of an efficient approach to the synthesis of a new monomer with non-symmetric structure is one of the main aims of the study. The presence of two nonequivalent propargyl groups in the desired monomer should be expected to affect the kinetics of polycycloaddition reaction and its direction, also the ratio of 1,4- and 1,5-disubstituted 1,2,3-triazole fractions in the AAC products[18] and the structure of obtained polymer.[18] So, investigation of the combined effect of different kinds of propargyl substituents on the rate and regioselectivity of APAPOT polycycloaddition is also an important goal of the study.

The reported[12] synthesis of azide-diacetylenic monomer ABPOT comprising replacement of chlorine atoms in cyanuric chloride with azide groups is characterized by a low yield due to spontaneous AAC reactions. Therefore, in this study, two different methods were tested to obtain APAPOT (see Scheme 1) when the last step was the quickest and mildest (as possible) introduction of azido group into the structure. Synthesis of APAPOT generally includes a series of reactions of successive chlorine atom substitution in cyanuric chloride for propargylamino, propargyloxy, and hydrazine groups, followed by nitrosation to azide. The difference in these methods consists in the order in which the propargylamino and propargyloxy groups are introduced into the structure of key trisubstituted *s*-triazine **3**. Method A is aimed at obtaining propargylamino-substituted



Scheme 1 *Reagents and conditions*: i, $HC{\equiv}CCH_2NH_2$, $NaHCO_3$, acetone–H_2O, 15 °C, 40 min; ii, $HC{\equiv}CCH_2OH$, NaOH, acetone–H_2O, 5 °C (for **2**) or room temperature (for **3**); iii, $HC{\equiv}CCH_2NH_2$, THF, room temperature, 2 weeks; iv, $N_2H_4{\cdot}H_2O$, Pr^iOH, reflux, 2 h; v, $NaNO_2$/HCl, H_2O, 0–5 °C, 30 min.

cyanuric chloride **1** first, and then the replacement of the rest chlorine atoms by propargyloxy groups to obtain compound **3**. Method B implied the obtaining tris(propargyloxy)-*s*-triazine **2** first, and then a selective substitution of one propargyloxy group for the propargylamino one. Method A looks more expedient since it provides 40% overall yield of APAPOT monomer over four synthesis steps, while the yield barely reaches 27% in case of method B. The structure and purity of all obtained compounds were determined and confirmed by IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, as well as elemental analysis (see Online Supplementary Materials). The resulting monomer possesses crystalline structure and has T_m = 130–131 °C, which is expected to be significantly higher than T_m of the ABPOT containing two propargyloxy groups, lower than that of the ABPAT, azido-bispropargylamine monomer, and, therefore, lower than the onset temperature of *s*-triazine-azide intense decomposition.[20–22]

To determine how the nature of substituent close to the triple bond affects the regioselectivity and rate of AAC reaction, quantum chemical study of the polycycloaddition mechanism of non-symmetric APAPOT and its symmetric counterparts, ABPOT and ABPAT, was carried out. Geometry optimization of monomers, transition states and products of dimerization reaction were investigated by DFT method at M06-2X/6-311++G(d,p) level of theory through Gaussian 09. The use of functional M06-2X and basis 6-311++G(d,p) allows one to explain non-covalent, including hydrogen, interactions well and gives estimated geometric parameters of azido groups closest to experimental data.[23–26] The QST3 approach was used to search for the transition state.[27,28] Once the transition state geometry has been found for each reaction, the Hessian was evaluated to ascertain that the geometry in fact is a transition state with exactly one imaginary frequency (see Online Supplementary Materials for optimized geometry of monomers, transition states and products of the investigated reactions).

Table 1 shows the values of the Gibbs free energy of the products ($\Delta G_{1.4}$, $\Delta G_{1.5}$), of the TS ($\Delta G^{\neq}_{1.4}$, $\Delta G^{\neq}_{1.5}$), and also the ratio of rate constants of 1,4- and 1,5-disubstituted 1,2,3-triazoles formation ($k_{1.5}/k_{1.4}$) during ABPOT, APAPOT and ABPAT polycycloaddition.

Comparing the $\Delta G^{\neq}$ values of AAC reactions of ABPOT, APAPOT and ABPAT monomers featuring azido and propargyloxy/propargylamino groups indicates that formation of 1,5-regioisomers proceeds most quickly for all monomers (see Table 1). The $k_{1.5}/k_{1.4}$ ratio of polycycloaddition rate constants increases in an ABPOT–APAPOT–ABPAT row by almost three orders of magnitude. The difference between the rates of obtaining different regioisomers should lead to the fact that the content of 1,5-disubstituted AAC products will be 83, 96.5 and 99.96%, respectively, and AAC reaction will be more and more regiospecific. That difference in reaction ways can be explained by special structure of transition states for APAPOT and ABPAT AAC reaction (Figure 1). Transition states are stabilized by hydrogen bond between the N***H*** of propargylamino group and the **N** atom of the *s*-triazine cycle.

Table 1 Kinetic parameters of ABPOT, ABPAT and APAPOT polycycloaddition obtained through DFT calculations.

Monomer	$\Delta G^{\neq}_{1.5}$/ kJ mol^{-1}	$\Delta G^{\neq}_{1.4}$/ kJ mol^{-1}	$k_{1.5}/k_{1.4}$	$\Delta G_{1.5}$/ kJ mol^{-1}	$\Delta G_{1.4}$/ kJ mol^{-1}
ABPOT	122.5	126.4	4.8	–212.8	–216.8
APAPOT_O[a]	122.4	130.6	26.8	–210.3	–221.4
APAPOT_N[b]	119.4	127.5	26.2	–211.7	–221.4
ABPAT	111.9	131.5	2767	–211.2	–223.4

[a] Reaction between propargyloxy and azido groups of monomer APAPOT.
[b] Reaction between propargylamino and azido groups of monomer APAPOT.

Detailed analysis of products of the APAPOT AAC reaction is of greatest interest, since both 1,4- and 1,5-disubstituted 1,2,3-triazoles can be formed as a result of azido groups interaction with triple bonds in propargyloxy (APAPOT_O) and propargylamino (APAPOT_N) groups. Based on $\Delta G^{\neq}_{1.4}$ and $\Delta G^{\neq}_{1.5}$ values of APAPOT_O and APAPOT_N, the propargylamino group is more reactive, since the rate constant ratio of propargylamino and propargyloxy groups in AAC reaction is ~3.4. It should be expected that triazole groups in APAPOT-based HBPs would consist of azido and propargylamino groups by ~70% (Figure 2).

It should be noted that the difference in the reactivity of propargyl groups is not severely crucial in terms of obtaining HBP based on this monomer. Calculation reveals that APAPOT-

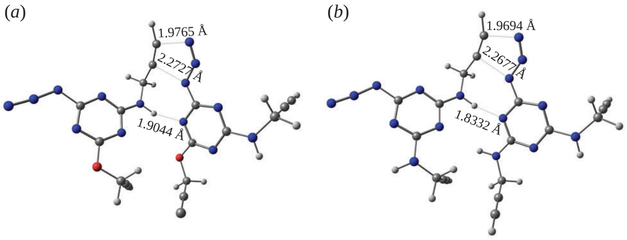


Figure 1 Structures of transition states for (*a*) APAPOT and (*b*) ABPAT AAC reaction with the formation of 1,5-disubstituted 1,2,3-triazoles featuring propargylamino group.

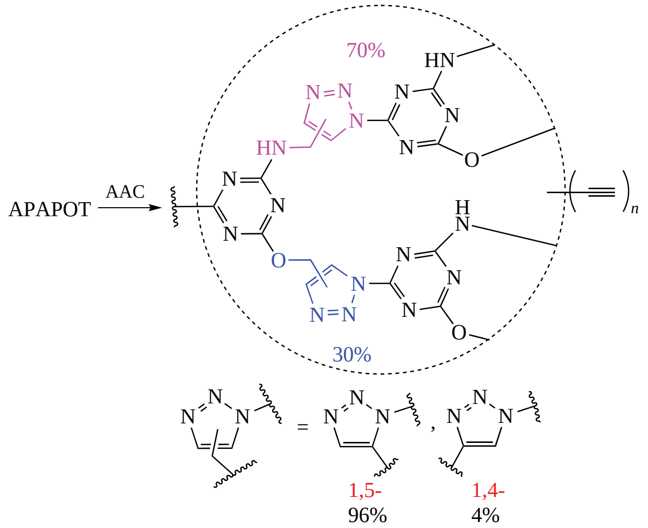


Figure 2 The predicted structure of APAPOT-based HBP.

based HBP degree of branching equals 0.42, while it is 0.5 for the case of AB_2 monomer random polycycloaddition (see Online Supplementary Materials). Considering the structure of 1,4- and 1,5-disubstituted 1,2,3-triazoles, we can conclude that the essential formation of 1,5-regioisomers upon AB_2 monomer polycycloaddition may contribute to a tighter packing of polymer macromolecules, and therefore, to HBPs obtaining with higher density. In this case, APAPOT-based HBPs should possess the highest density that, without any doubts, would have a further positive effect on the specific energy characteristics of triazine-triazole HBPs.

In conclusion, we have developed an efficient synthesis of a new azido-diacetylenic monomer of the ABB′ type, namely, 2-azido-4-propargylamino-6-propargyloxy-*s*-triazine. It can serve as a base for obtaining new high-enthalpy HBPs. DFT study of its polycycloaddition mechanism showed that the process should occur with the selective formation of 1,5-disubstituted 1,2,3-triazoles, and the difference in reactivity of propargyloxy and propargylamino groups does not exceed 3.5 times towards propargylamino group.

This work was performed in accordance with the state tasks no. 0089-2019-0008 (state registration no. AAAA-A19-119041090087-4), no. 0074-2019-0014 (AAAA-A19-119101590029-0), no. 0089-2019-0005 (AAAA-A19-119101690058-9), using the equipment of the Multi-User Analytical Center of IPCP RAS.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.07.012.

References

1 A. V. Sheremetev, *Mendeleev Commun.*, 2020, **30**, 490.
2 C. S. Pant, R. M. Wagh, J. K. Nair, G. M. Gore, M. Thekkekara and S. Venugopalan, *Propellants, Explos., Pyrotech.*, 2007, **32**, 461.
3 A. E. Tarasov, E. O. Perepelitsina, L. B. Romanova, A. V. Darovskikh, V. S. Smirnov, E. R. Badamshina and Yu. M. Mikhailov, *Mendeleev Commun.*, 2022, **32**, 341.
4 E. Sagot, A. Le Roux, C. Soulivet, E. Pasquinet, D. Poullain, E. Girard and P. Palmas, *Tetrahedron*, 2007, **63**, 11189.
5 G. He, X. Li, L. Bai, L. Meng, Y. Dai, Y. Sun, C. Zeng, Z. Yang and G. Yang, *Composites, Part B*, 2020, **191**, 107967.
6 V. V. Zakharov, N. V. Chukanov, T. S. Larikova, G. V. Shilov, A. G. Korepin, A. N. Pivkina, K. A. Monogarov, B. L. Korsunskiy, D. V. Korchagin and S. M. Aldoshin, *Russ. Chem. Bull.*, 2020, **69**, 118.
7 X. Zang, H. Liu, Q. Li, Z. Li and Z. Li, *Polym. Chem.*, 2020, **11**, 5493.
8 A. Pacini, A. Nitti, G. Sangiovanni, M. Vitale and D. Pasini, *J. Polym. Sci.*, 2021, **59**, 2014.
9 H. Rezania, *Des. Monomers Polym.*, 2020, **23**, 83.
10 H. J. Jeong and B. K. Kim, *React. Funct. Polym.*, 2017, **116**, 92.
11 S. V. Karpov, E. O. Perepelitsina and G. V. Malkov, *Polym. Sci., Ser. B*, 2014, **56**, 298.
12 G. V. Malkov, A. V. Shastin, Y. I. Estrin, E. R. Badamshina and Y. M. Mikhailov, *Propellants, Explos., Pyrotech.*, 2008, **33**, 431.
13 M. H. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya and R. Gilardi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4928.
14 J. Li, S. Wang, L. Liao, Q. Ma, Z. Zhang and G. Fan, *New J. Chem.*, 2019, **43**, 10675.
15 A. V. Shastin, A. O. Petrov, G. V. Malkov and T. N. Gavrishova, *Chem. Heterocycl. Compd.*, 2021, **57**, 866.
16 S. V. Karpov, A. O. Petrov, G. V. Malkov and E. R. Badamshina, *Mendeleev Commun.*, 2022, **32**, 338.
17 A. O. Petrov, G. V. Malkov, S. V. Karpov, A. V. Shastin and A. V. Bakeshko, *Key Eng. Mater.*, 2019, **816**, 151.
18 R. Huisgen, *Angew. Chem., Int. Ed.*, 1963, **2**, 565.
19 S. V. Karpov, A. G. Iakunkov and G. V. Malkov, *Key Eng. Mater.*, 2019, **816**, 339.
20 S. P. Green, A. D. Payne, K. M. Wheelhouse, J. P. Hallett, P. W. Miller and J. A. Bull, *J. Org. Chem.*, 2019, **84**, 5893.
21 M. H. Rao, V. D. Ghule and K. Muralidharan, *J. Chem. Sci.*, 2021, **133**, 1.
22 D. Chen, H. Yang, Z. Yi, H. Xiong, L. Zhang, S. Zhu and G. Cheng, *Angew. Chem., Int. Ed.*, 2018, **57**, 2081.
23 B. J. Cabral and M. L. Costa, *J. Mol. Struct.: THEOCHEM*, 1995, **343**, 31.
24 S. V. Karpov, V. P. Lodygina and G. V. Malkov, *J. Appl. Spectrosc.*, 2014, **81**, 23 (*Zh. Prikl. Spektrosk.*, 2014, **81**, 26).
25 Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2008, **4**, 1849.
26 A. J. Cohen, P. Mori-Sánchez and W. Yang, *Chem. Rev.*, 2012, **112**, 289.
27 C. Peng and H. B. Schlegel, *Isr. J. Chem.*, 1993, **33**, 449.
28 C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.*, 1996, **17**, 49.

Received: 24th November 2021; Com. 21/6759