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Bis(triazole) derivatives of organodigermanes: synthesis, structure, and properties

Kirill V. Zaitsev,* Andrei D. Trubachev, Victor A. Tafeenko and Yurii F. Oprunenko

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: zaitsev@org.chem.msu.ru

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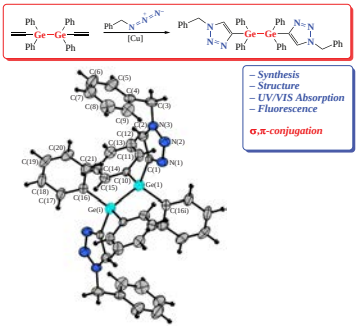
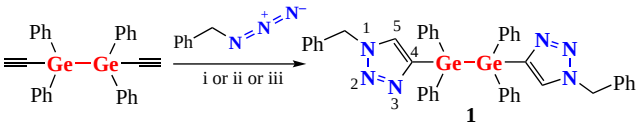
The synthesis and molecular structure of the triazole-containing organodigermane [(4,1-BnC$_2$HN$_3$)Ph$_2$Ge]$_2$ (C$_2$HN$_3$ is 1,2,3-triazole-4,1-diyl) obtained under various conditions of the copper(I)–azide/alkyne cycloaddition are reported. Effective σ,π-conjugation in the compound between Ge–Ge, aryl and heterocyclic groups was established. The optical properties (absorption and fluorescence) of the digermane in MeCN and MeCN/H$_2$O were evaluated, indicating the influence of the solvent.



Keywords: organogermanium compounds, click chemistry, group 14 elements, XRD analysis, optical properties.

Organogermanium compounds attract considerable attention due to broad fundamental interest[1–5] as well as due to their application in organic synthesis,[6–9] catalysis,[10] medicine,[11,12] ligand design,[13] activation of small molecules,[14] material chemistry,[15] organic electronics,[16] production of optical and electrical devices.[17–19] A special place among these derivatives is occupied by oligoorganogermanes,[20] molecular compounds with Ge–Ge bonds possessing σ-conjugation. Introduction of aryl groups at the Ge atoms makes it possible to increase conjugation in the molecule (σ,π-conjugation), which is promising for practical applications (changes in the electronic states of the molecule, the energies of their frontier orbitals).[21,22] The development of efficient syntheses for obtaining functionalized organogermanium compounds is of high current interest. The use of [3+2] cycloaddition click-chemistry reaction[23,24] for construction of heterocyclic organogermanium compounds[25] is a powerful strategy in the chemistry of group 14 elements, which allows one to access organometallic heterocyclic compounds hard-to-obtain by other methods.

The purpose of this work was the synthesis of a model bistriazolyl digermane **1**, [(4,1-BnC$_2$HN$_3$)Ph$_2$Ge]$_2$ (C$_2$HN$_3$ is 1,2,3-triazole-4,1-diyl), using CuAAC (copper catalyzed azide–alkyne cycloaddition) catalyst systems, alternative to those previously used, and to study its structure and optical properties



1

84% (i, ref. 25)
41% (ii, this work)
28% (iii, this work)

Scheme 1 *Reagents and conditions*: i, CH$_2$Cl$_2$, Et$_3$N, CuBr (10 mol%); ii, Cu(OAc) (10 mol%), THF; iii, sodium ascorbate (20 mol%), CuSO$_4$·5H$_2$O (10 mol%), H$_2$O–THF (1:1).

in polar solvents. Previously,[25] we developed an effective method for the synthesis of bis(triazole) derivative of organodigermanes as a result of [3+2] cycloaddition of [(HC≡C)Ph$_2$Ge]$_2$ and RCH$_2$N$_3$ (R = Alk, Ar) (Scheme 1, conditions i). The procedure involved the use of a CuBr/Et$_3$N/CH$_2$Cl$_2$ catalytic system, which ensured the homogeneity of the mixture and the controlled character of the reaction. As alternatives, in this work we tested CuOAc and CuSO$_4$·5H$_2$O (see Scheme 1, conditions ii and iii, respectively). A common feature of these syntheses is the formation of a 1,4-substituted triazolyl ring.

The use of CuOAc allows the reaction to be carried out without an external base.[26,27] It turned out that the target compound **1** was isolated in moderate yield (41%) only after flash column chromatography (in contrast to our conditions found earlier[25] when simple recrystallization was sufficient for the synthesis of a pure substance) due to the complex composition of the reaction mixture. Under typical CuAAC conditions (CuSO$_4$·5H$_2$O, sodium ascorbate, water, THF),[28] final column chromatography afforded the target product **1** also in moderate yield (28%). In this case, the conversion (80%) is due to the heterogeneity of the reaction mixture. A comparison of the three catalytic systems (see Scheme 1) clearly indicates that the use of CuBr/Et$_3$N/CH$_2$Cl$_2$ is the best choice for CuAAC reactions in the case of group 14 elements derivatives.

The molecular structure of compound **1** was studied in crystal by XRD analysis (Figure 1).† In general, the molecular structure

† *Crystal data for* **1**. C$_{21}$H$_{18}$GeN$_3$ (M = 384.97), monoclinic, space group $P2_1/n$, Z = 4, d_{calc} = 1.395 g cm^{-3}, abs. coeff. 1.678 mm^{-1}, F(000) 788, T = 295(2) K, a = 12.5847(8), b = 9.0929(5) and c = 16.1645(9) Å, β = 97.697(3)°, V = 1833.06(19) Å^3. A total of 24403 reflections (θ range 2.200–26.999°) were collected, and 3995 independent reflections, R_1 = 0.0511, wR_2 = 0.0808, goodness of fit on F^2 0.889. The structure was solved and refined using the SHELXTL program package. The structure was defined by direct statistical methods and refined by full-matrix anisotropic approximation for F^2 for all non-hydrogen atoms with

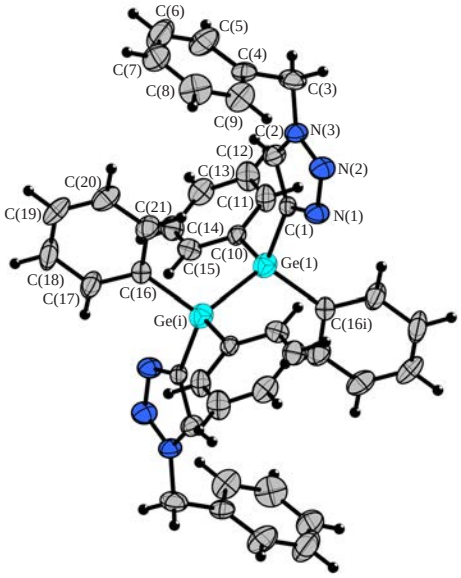


Figure 1 Molecular structure of $[(4,1\text{-}BnC_2HN_3)Ph_2Ge]_2$ (**1**). Selected bond lengths (Å) and angles (°): Ge(1)–Ge(i) 2.4303(11), Ge(1)–C(10) 1.943(5), Ge(i)–C(16) 1.949(5), Ge(1)–C(1) 1.962(5); C(10)–Ge(1)–C(16i) 108.8(2), C(10)–Ge(1)–C(1) 106.3(2), C(16i)–Ge(1)–C(1) 109.7(2), C(10)–Ge(1)–Ge(i) 113.05(16), C(16)–Ge(i)–Ge(1) 110.72(14), C(1)–Ge(1)–Ge(i) 108.21(14).

of compound **1** is similar to those of other triazolyl-containing oligoorganogermanes $\{[4,1\text{-}(RCH_2)C_2HN_3]Ph_2Ge\}_2$ (R = C_6H_4Br-*p*, $CH_2OC_6H_4CHO$-*p*, $CH_2OC_6H_4COOMe$-*p*) studied previously,[25] where *l*(Ge–Ge) = 2.4303(11) Å, $l(Ge–C_{Ph})_{av}$ = 1.946(5) Å and $l(Ge–C_{Triazol})$ = 1.962(5) Å. The molecule of **1** in the crystal is centrosymmetric (the center of symmetry lies on the Ge–Ge bond) with two identical parts; triazolyl rings are in the N-*transoid* conformation (dihedral C_N–Ge–Ge–C_N angle, 180°). In space, the molecule has staggered (*anti*-planar) conformation (torsion angles C–Ge–Ge–C are 59.06/60.94°; ideal torsion 60°). Interestingly, triazolyl rings and symmetrical Ph rings lie in parallel planes. Analysis of the bond angles between Ph_{CH2} planes and triazolyl rings (74.40°) may indicate conjugation (ideally 90°), which was previously established[25] by electrochemical and optical methods. So, in general, in the molecule there is a σ,π-conjugation between Ge–Ge, Ph and triazolyl groups.

The optical properties of compound **1** were studied in a polar solvent (MeCN) and in MeCN/H_2O mixtures to investigate the effect of solvent polarity. The UV/VIS absorption spectra of **1** in MeCN and in MeCN with added water (up to 40%) are presented in Figure 2. Despite the nonpolar nature of **1** (oligoorganotetrelanes are analogues of alkanes), it is soluble in these mixtures in quantities sufficient to record spectra under these homogeneous solutions. It can be seen that an increase in water content led to a decrease in molar absorption due to a decrease in concentration. Interestingly, absorption in MeCN is observed at λ_{max} = 234 nm ($\varepsilon = 1.3 \times 10^4$ dm^3 mol^{-1} cm^{-1}), 263 nm ($\varepsilon = 0.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}), which is close to the data[25] for **1** in CH_2Cl_2 [λ_{max} = 234 nm ($\varepsilon = 3.4 \times 10^4$ dm^3 mol^{-1} cm^{-1}), 262 nm ($\varepsilon = 0.3 \times 10^4$ dm^3 mol^{-1} cm^{-1})]. The transition from CH_2Cl_2 to MeCN only resulted in a decrease in molar absorptivity.

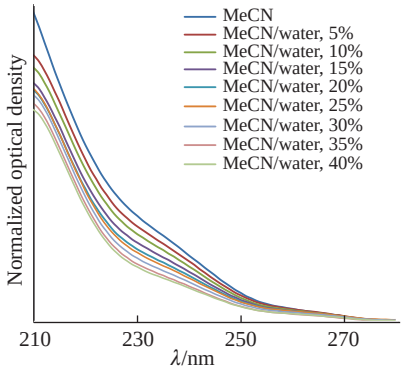


Figure 2 Normalized UV/VIS absorption of compound **1** in acetonitrile and in acetonitrile/water mixtures.

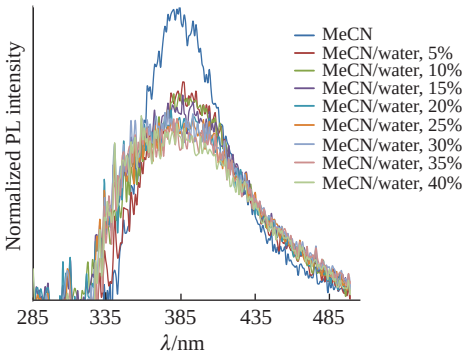


Figure 3 Normalized fluorescence spectra of compound **1** in MeCN and in MeCN/water mixtures.

Fluorescence of bistriazolyl digermane **1** in MeCN is observed at λ_{max} = 385 nm (λ_{ex} = 277 nm) (Figure 3); with increasing water content, luminescence intensity decreases, but increasing water content does not significantly change the emission parameters. Indeed, the fluorescence quantum yield in MeCN is 6.7% and remains virtually unchanged with increasing water content. However, this value exceeds the quantum yield in CH_2Cl_2 (0.2%), which indicates the influence of increasing solvent polarity on luminescence efficiency for oligoorganogermanes; this phenomenon was revealed for the first time. In addition, in CH_2Cl_2 fluorescence of **1** is observed in the bluer region at λ_{max} of 320 and 359 nm (λ_{ex} = 280 nm).

To summarize, among various reported CuAAC procedures for the synthesis of germanium triazoles, the CuBr/Et_3N/CH_2Cl_2 system is optimal in terms of yield of the target compounds. Changing the substituent at position 4 of the triazolyl ring in bis(triazole) derivatives of organodigermanes has little effect on geometric parameters of the molecule; this leads to the need for the synthesis of aryl derivatives, where Ar is conjugated with other chromophores. In this work, it was established that a polar solvent (acetonitrile and its mixtures with water) significantly changes the emission properties of molecular triazolyl oligoorganogermanes (increased Stokes shift and quantum yield). Further research is ongoing on the synthesis of functionalized organogermanium compounds and the study of their promising properties (optical, semiconductor, and nonlinear optic).

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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.2024.10.016.

ShelXL program. The hydrogen atoms were localized by direct method and refined in the isotropic approximation.

CCDC 2363351 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

References

1 K. V. Zaitsev, in *Organogermanium Compounds: Theory, Experiment, and Applications*, ed. V. Ya. Lee, Wiley, 2023, vol. 1, ch. 2, pp. 103–193; https://doi.org/10.1002/9781119613466.ch2.

2 A. I. Fedulin, Yu. F. Oprunenko, S. S. Karlov, G. S. Zaitseva and K. V. Zaitsev, *Mendeleev Commun.*, 2021, **31**, 850; https://doi.org/10.1016/j.mencom.2021.11.027.

3 V. Ya. Lee, *Molecules*, 2023, **28**, 1558; https://www.mdpi.com/1420-3049/28/4/1558.

4 V. Ya. Lee, *Mendeleev Commun.*, 2023, **33**, 145; https://doi.org/10.1016/j.mencom.2023.02.001.

5 I. S. Ignatyev, Yu. A. Kondratenko, D. V. Lezov, V. L. Ugolkov and T. A. Kochina, *Mendeleev Commun.*, 2023, **33**, 601; https://doi.org/10.1016/j.mencom.2023.09.003.

6 C. Fricke and F. Schoenebeck, *Acc. Chem. Res.*, 2020, **53**, 2715; https://doi.org/10.1021/acs.accounts.0c00527.

7 T. Rogova, E. Ahrweiler, M. D. Schoetz and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2024, **63**, e202314709; https://doi.org/10.1002/anie.202314709.

8 E. Ahrweiler, M. D. Schoetz, G. Singh, Q. P. Bindschaedler, A. Sorroche and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401545; https://doi.org/10.1002/anie.202401545.

9 Q.-H. Xu and B. Xiao, *Org. Chem. Front.*, 2022, **9**, 7016; https://doi.org/10.1039/D2QO01467J.

10 D. Basu, B. Ghosh, D. Srivastava, N. Patra and H. P. Nayek, *Dalton Trans.*, 2024, **53**, 5648; https://doi.org/10.1039/D4DT00239C.

11 T. Nakamura, Y. Shimada and K. Sato, in *Organogermanium Compounds: Theory, Experiment, and Applications*, ed. V. Ya. Lee, Wiley, 2023, vol. 1, ch. 19, pp. 839–865; https://doi.org/10.1002/9781119613466.ch19.

12 T. Takeda, S. Doiyama, J. Azumi, Y. Shimada, Y. Tokuji, H. Yamaguchi, K. Nagata, N. Sakamoto, H. Aso and T. Nakamura, *Sci. Rep.*, 2019, **9**, 13637; https://doi.org/10.1038/s41598-019-49883-7.

13 J. A. Cabeza and P. García-Álvarez, *Chem. – Eur. J.*, 2024, **30**, e202400786; https://doi.org/10.1002/chem.202400786.

14 K. V. Zaitsev, A. D. Trubachev and O. Kh. Poleshchuk, *Int. J. Mol. Sci.*, 2023, **24**, 10218; https://doi.org/10.3390/ijms241210218.

15 K. V. Zaitsev, I. S. Makarov, Y. F. Oprunenko, V. A. Tafeenko, E. Kh. Lermontova and A. V. Churakov, *Int. J. Mol. Sci.*, 2023, **24**, 13575; https://doi.org/10.3390/ijms241713575.

16 K. V. Zaitsev, V. A. Tafeenko, Y. F. Oprunenko, A. V. Kharcheva, Z. Zhanabil, Y. Suleimen, K. Lam, V. B. Zaitsev, A. V. Zaitseva, G. S. Zaitseva and S. S. Karlov, *Chem. – Asian J.*, 2017, **12**, 1240; https://doi.org/10.1002/asia.201700151.

17 G.-H. Lee, M.-C. Sung, Y. S. Kim, B. Ju and D.-W. Kim, *ACS Nano*, 2020, **14**, 15894; https://doi.org/10.1021/acsnano.0c07262.

18 T. A. Su, H. Li, R. S. Klausen, N. T. Kim, M. Neupane, J. L. Leighton, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *Acc. Chem. Res.*, 2017, **50**, 1088; https://doi.org/10.1021/acs.accounts.7b00059.

19 T. A. Su, H. Li, V. Zhang, M. Neupane, A. Batra, R. S. Klausen, B. Kumar, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *J. Am. Chem. Soc.*, 2015, **137**, 12400; https://doi.org/10.1021/jacs.5b08155.

20 C. S. Weinert, in *Organogermanium Compounds: Theory, Experiment, and Applications*, ed. V. Ya. Lee, Wiley, 2023, vol. 1, ch. 18, pp. 787–837; https://doi.org/10.1002/9781119613466.ch18.

21 K. V. Zaitsev, K. Lam, O. Kh. Poleshchuk, L. G. Kuz'mina and A. V. Churakov, *Dalton Trans.*, 2018, **47**, 5431; https://doi.org/10.1039/C8DT00256H.

22 C. Marschner and J. Hlina, in *Comprehensive Inorganic Chemistry II*, eds. J. Reedijk, K. Poeppelmeier and T. Chivers, Elsevier, Amsterdam, 2013, vol. 1, pp. 83–117; https://doi.org/10.1016/B978-0-08-097774-4.00104-2.

23 E. Haldón, M. C. Nicasio and P. J. Pérez, *Org. Biomol. Chem.*, 2015, **13**, 9528; https://doi.org/10.1039/C5OB01457C.

24 M. Meldal and F. Diness, *Trends Chem.*, 2020, **2**, 569; https://doi.org/10.1016/j.trechm.2020.03.007.

25 K. V. Zaitsev, G. A. Veshchitsky, Y. F. Oprunenko, A. V. Kharcheva, A. A. Moiseeva, I. P. Gloriozov and E. Kh. Lermontova, *Chem. – Asian J.*, 2023, **18**, e202300753; https://doi.org/10.1002/asia.202300753.

26 C. Shao, G. Cheng, D. Su, J. Xu, X. Wang and Y. Hu, *Adv. Synth. Catal.*, 2010, **352**, 1587; https://doi.org/10.1002/adsc.200900768.

27 Q. Zhang, X. Wang, C. Cheng, R. Zhu, N. Liu and Y. Hu, *Org. Biomol. Chem.*, 2012, **10**, 2847; https://doi.org/10.1039/C2OB06942C.

28 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596; https://doi.org/10.1002/1521-3773(20020715)41:14<2596::AID-ANIE2596>3.0.CO;2-4.

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