molbank

MDPI

Short Note

3-(4-Ethynylphenyl)-1,5-diphenylformazan

Ida A. Lupanova [1], Dzhamilya N. Konshina [1], Igor V. Sukhno [2], Ekaterina S. Spesivaya [1] and Valery V. Konshin [1,*]

[1] Department of Chemistry and High Technology, Kuban State University, 149 Stavropolskaya Str., 350040 Krasnodar, Russia; konovalova_ida@mail.ru (I.A.L.); jfox@list.ru (D.N.K.); ekaterina-1305@mail.ru (E.S.S.)

[2] Nanobiotechnology Department, Kuban State Agrarian University, 13 Kalinina Str., 350044 Krasnodar, Russia; sukhno_igor@mail.ru

* Correspondence: organotin@mail.ru; Tel.: +7-(908)-68-228-74

Abstract: The structure of the "clickable" formazan, 3-(4-ethynylphenyl)-1,5-diphenylformazan, has been determined for the first time in a single crystal. The synthesis of 3-(4-ethynylphenyl)-1,5-diphenylformazan was carried out by coupling 4-(trimethylsilyl)ethynylbenzaldehyde phenylhydrazone with diazotized aniline, followed by desilylation, with a total yield of 54%.

Keywords: formazan; clickable dyes; single crystal X-ray diffraction

1. Introduction

The interest in formazans is due to the presence of a set of practically important properties, which are rarely manifested simultaneously in representatives of other classes of organic compounds [1–5]. Formazans can exhibit photo- and thermochromic properties, act as effective metal ligands or indicators of redox processes, and also demonstrate various types of biological activity. Their applications include use as dyes, indicators, components of optical recording media and photographic compositions, and catalysts for oxidation–reduction reactions. Formazans are also applied in fine organic synthesis; they are particularly important as starting compounds for the synthesis of tetrazolium salts [6–10], verdazyls [11–14], and boratetrazines [15–21] (Figure 1), as well as various heterocycles [22,23].

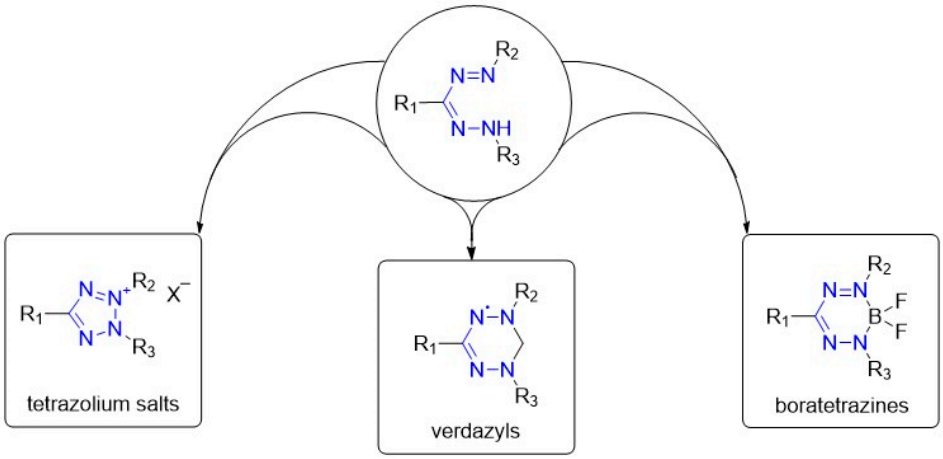


Figure 1. Synthetic potential of formazans.

The structural diversity of formazans is due to the ease of varying the three substituents in the azo-hydrazone chain. Of particular interest are "clickable" formazans, which can be

Academic Editor: René T. Boeré

Received: 10 February 2025
Revised: 19 February 2025
Accepted: 24 February 2025
Published: 3 March 2025

Citation: Lupanova, I.A.; Konshina, D.N.; Sukhno, I.V.; Spesivaya, E.S.; Konshin, V.V. 3-(4-Ethynylphenyl)-1,5-diphenylformazan. *Molbank* **2025**, *2025*, M1976. https://doi.org/10.3390/M1976

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

used to synthesis conjugates with various molecules and to functionalize solid matrices. To date, several "clickable" formazans have been described [24–30] (Figure 2). One of the simplest compounds of this type, containing an ethynyl group in the meso position of the azo-hydrazone chain, is 3-(4-ethynylphenyl)-1,5-diphenylformazan 2, which was recently synthesized for the first time by coupling 4-ethynylbenzaldehyde phenylhydrazone with phenyldiazonium tosylate [27] and used for the synthesis of verdazyls.

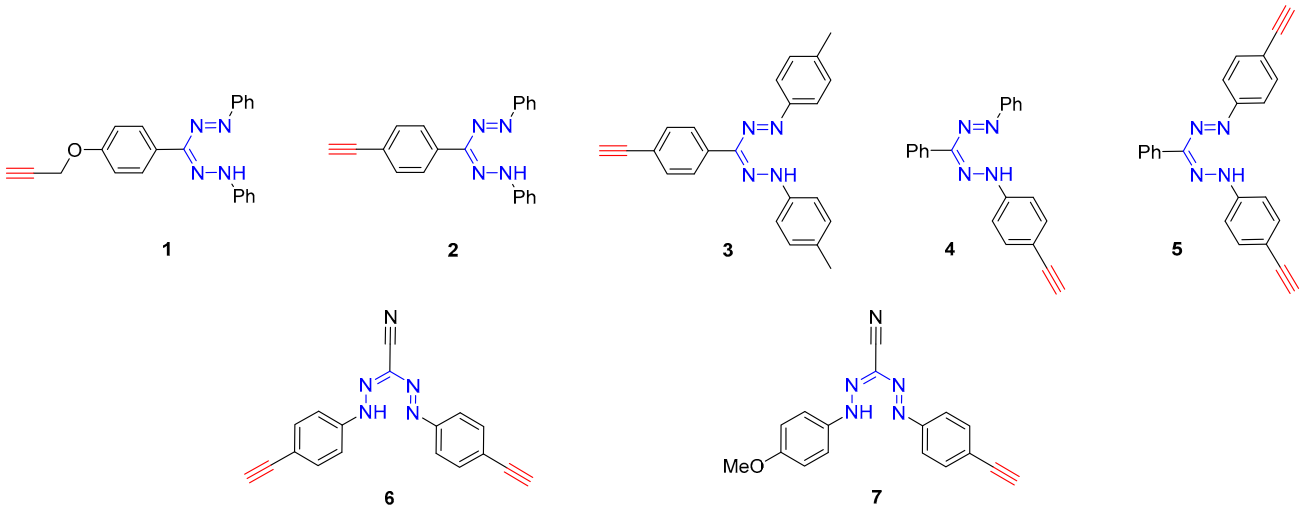
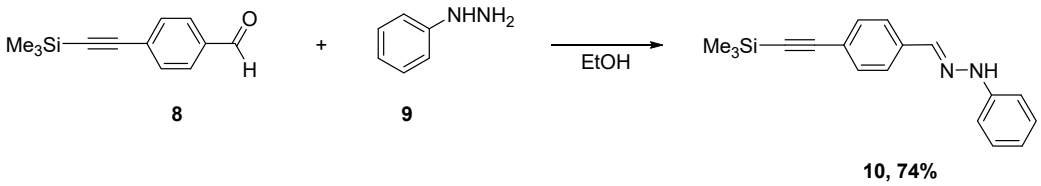


Figure 2. Some clickable formazans (**1** [24–26], **2** [27], **3** [28], **4**, **5** [29], **6**, **7** [30]).

The present work describes the synthesis of 3-(4-ethynylphenyl)-1,5-diphenylformazan and its crystal structure.

2. Results and Discussion

As the starting building block, we used the readily available compound 4-(trimethylsilyl) ethynylbenzaldehyde (**8**) [31], which is also a commercially available reagent ($6.03/1 g Macklin Inc., Rochelle, IL, USA). When compound **8** was reacted with phenylhydrazine in boiling ethanol, 1-phenyl-2-[4-((trimethylsilyl)ethynyl)benzylidene]hydrazine (**10**) was synthesized, with a yield of 74% (Scheme 1).

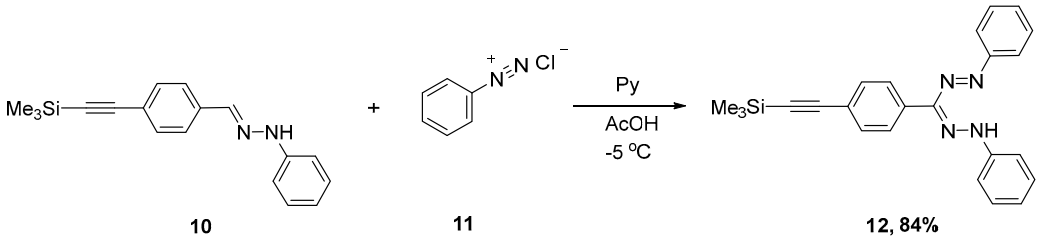


Scheme 1. Reaction of 4-(trimethylsilyl)ethynylbenzaldehyde (**8**) with phenylhydrazine (**9**).

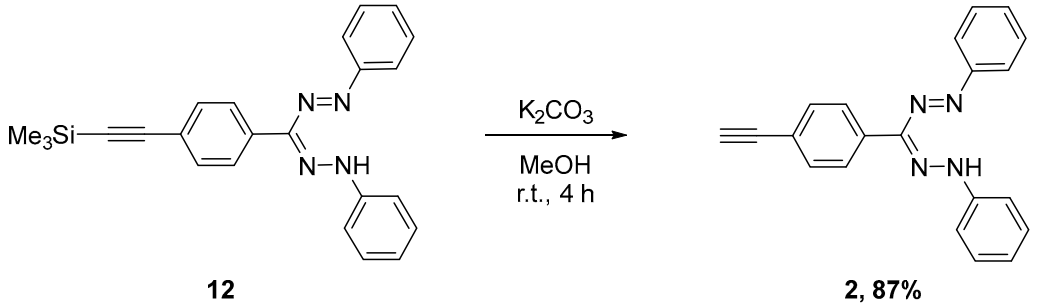
For the synthesis of formazan, a classical scheme was chosen involving the condensation of the phenylhydrazone with the diazonium salt in a pyridine medium in the presence of glacial acetic acid. The reaction was carried out at −5 °C (Scheme 2). According to TLC data, the product (**12**) formed is sufficiently pure and does not require additional purification.

Desilylation of **12** was performed using potassium hydroxide in methanol at room temperature (Scheme 3).

The structure of products **10, 12, and 2** was confirmed by ^{1}H, ^{13}C NMR, IR spectroscopy and mass spectrometry.



Scheme 2. The reaction of 1-phenyl-2-[4-((trimethylsilyl)ethynyl)benzylidene]hydrazine (**10**) with phenyldiazonium chloride (**11**).



Scheme 3. Desilylation of 1,5-diphenyl-3-[4-((trimethylsilyl)ethynyl)phenyl]formazan.

The structure of 3-(4-ethynylphenyl)-1,5-diphenylformazan (**2**) was unambiguously confirmed by single-crystal X-ray analysis (Figure 3). The single crystals of **2** were grown by recrystallization of the title compound in ethanol.

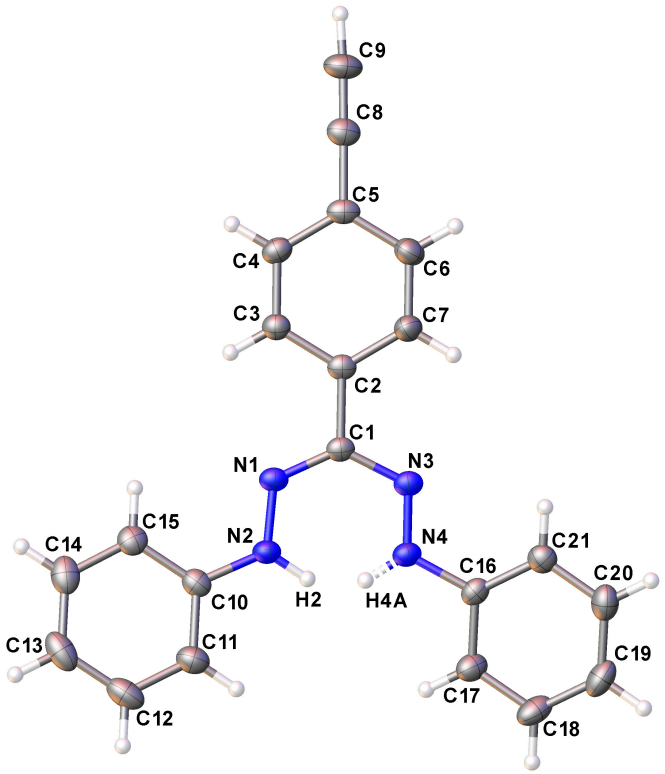


Figure 3. Crystal structure of compound **2** with labeling schemes and 50% thermal ellipsoids.

Compound **2** crystallizes in the centrosymmetric orthorhombic space group Pbca. The whole molecule is non-planar, with the aryl rings slightly twisted with respect to the formazan plane N2N1C1N3N4. The dihedral angles between the aromatic planes C2–C7, C10–C15, C16–C21 and the plane N2N1C1N3N4 are 5.8 °, 10.2 °, and 15.4 °,

respectively. The formazan system has the *syn*,*s-cis* configuration, which is characteristic of some other triaryl substituted formazans [16,17]. The difference between the lengths of the double and single bonds in the formazan moiety is reduced, indicating π-electron density delocalization (e.g., N4 = N3 1.288 (1) Å, N1–N2 1.314 (1) Å). A similar distribution of bond lengths is observed in other triaryl-substituted formazans (e.g., CSD refcodes: PEVWET [16], PUVCOA [17]). Thus, the ethynyl substituent does not affect the structure of the formazan moiety but makes the arrangement of the aryl rings more twisted compared to the PEVWET [16] and PUVCOA [17], probably due to the packing features of the ethynyl compound. The hydrogen atom of the NH group is refined as disordered over two positions with occupancies of 0.69 (2) for H2 and 0.31 (2) for H4A. The syn, s-cis configuration is stabilized by intramolecular hydrogen bonds N2–H2···N4 (N2–H2 0.89 (2) Å, H2···N4 1.86 (2) Å), and N4–H4A···N2 (N4–H4A 0.89 (5) Å, H4A···N2 1.87 (6) Å) for the minor disorder component.

In conclusion, 3-(4-ethynylphenyl)-1,5-diphenylformazan was synthesized, and its structure was confirmed by a combination of ^{1}H, ^{13}C NMR, IR spectroscopy, mass spectrometry, and X-ray diffraction data.

3. Materials and Methods

The reactions were monitored by thin-layer chromatography (Sorbfil, Imid Ltd., Krasnodar, Russia). The ^{1}H-NMR and ^{13}C-NMR spectra were acquired on ECA400 (JEOL, Tokyo, Japan) (400 and 100 MHz, respectively) spectrometers in $CDCl_3$ and $(CD_3)_2SO$ at room temperature. The chemical shifts δ were measured in ppm with reference to the residual solvent resonances (^{1}H: $CDCl_3$, δ = 7.25 ppm; ^{13}C: $CDCl_3$, δ = 77.2 ppm; ^{1}H: $(CD_3)_2SO$, δ = 2.49 ppm; ^{13}C: $(CD_3)_2SO$, δ = 39.5 ppm) or Me_4Si. The splitting patterns are referred to as s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (*J*) are given in hertz. IR spectra were recorded on an IR Prestige (Shimadzu, Kyoto, Japan), using tablets of samples with KBr. High-resolution and accurate mass measurements were carried out using a Bruker MaXis Impact (electrospray ionization/time of flight) (Bruker, Bremen,_Germany). The melting points were determined on a Stuart SMP30 apparatus and left uncorrected. X-ray diffraction investigation of compound 2 was conducted using an automatic diffractometer Bruker Apex DUO (CuKα radiation, ω- and φ-scanning). Empirical absorption correction and systematic error correction were performed using the SADABS program [32]. The structure was deciphered by direct methods and refined using the least squares method in the anisotropic full-matrix approximation based on F2hkl. The positions of hydrogen atoms bonded to nitrogen atoms and the carbon atom of the acetylene fragment were determined from difference Fourier syntheses of electron density, while the positions of the remaining hydrogen atoms were calculated. All hydrogen atoms, except for the one bonded to the nitrogen atom, were refined in the riding model with Uiso(H) = 1.2Ueq(C). All calculations were performed using the SHELXTL PLUS software package [33].

The commercial reagents employed in the synthesis were 4-(trimethylsilyl) ethynylbenzaldehyde (95%, Manchester Organics Ltd., Runcorn, UK), Phenylhydrazine (for synthesis, ≥97%, Aldrich, St. Louis, MO, USA), and aniline (≥99%, Vekton, Saint Petersburg, Russia).

*3.1. 1-Phenyl-2-[4-((trimethylsilyl)ethynyl)benzylidene]hydrazine (***10***)*

In a reflux flask with a condenser, 20 mL of ethanol, 1 g (4.94 mmol) of 4-(trimethylsilyl)ethynylbenzaldehyde, and 485 μL (4.94 mmol) of phenylhydrazine were added and heated for 20 min. The reaction mixture was cooled to 3 °C for crystallization. The precipitate was filtered and washed with a small amount of cold ethanol.

Yield: 1.07 g (74%); beige crystals; mp 132-135 °C. IR (KBr): ν = 3311 (NH), 3078, 3049, 3034 (Csp^2-H), 2954, 2897 (Csp^3-H), 2154 (Csp-Csp), 1598, 1589, 1523, 1494 (Csp^2-Csp^2), 1444, 1408, 1355, 1313, 1296, 1261, 1249, 1222, 1134, 1102, 1068, 920, 864, 846, 835 cm^{-1} (SI, Figure S1). ^1H NMR ($CDCl_3$, 399.78 MHz): δ = 0.26 (s, 9H, CH_3), 6.86–6.90 (m, 1H, CH), 7.08–7.12 (m, 2H, CH), 7.24–7.30 (m, 2H, CH), 7.43–7.46 (m, 2H, CH), 7.55–7.59 (m, 2H, CH + 1H CH) (SI, Figure S2). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = −0.03 (CH_3), 95.4 (Csp), 105.1 (Csp), 112.8 (CH), 120.3 (CH), 122.7 (C), 125.8 (CH), 129.3 (CH), 132.2 (CH), 135.4 (C), 136.2 (CH_{imine}), 144.3 (C) (SI, Figure S3). UV–VIS λmax, nm (Irel, %): 252 (6671), 372 (11396). HRMS ESI TOF: m/z = 293.1476 $[M+H]^+$ (293.1468 calcd. for $C_{18}H_{21}N_2Si$) (SI, Figure S4).

*3.2. 1,5-Diphenyl-3-[4-((trimethylsilyl)ethynyl)phenyl]formazan (***12***)*

To a solution of 0.46 g (1.57 mmol) of 1-phenyl-2-[4-((trimethylsilyl)ethynyl) benzylidene]hydrazine in 15 mL of pyridine and 0.5 mL of glacial acetic acid, a solution of phenyl diazonium chloride, synthesized from 143 μL (1.57 mmol) of aniline, 0.108 g (1.57 mmol) of $NaNO_2$, and 1.2 mL of 37% HCl in 1 mL of water, was added at −5 °C. The resulting cherry–red reaction mixture with precipitate was maintained for 30 min at −5 °C, and then for 1 h at room temperature. The reaction mixture was then poured into 150 mL of 2M HCl, and the precipitate was filtered and washed with water. Yield: 525 mg (84%); cherry–red powder; mp 193-195 °C. Rf = 0.41 (Hexane–EtOAc 10:1). IR (KBr): ν = 3084, 3064, 3049, 3032 (Csp^2-H), 2954 (Csp^3-H), 2152 (Csp-Csp), 1597, 1506, 1498 (Csp^2-Csp^2), 1452, 1404, 1354, 1313, 1249, 1236, 1186, 1074, 1035, 866, 842 cm^{-1} (SI, Figure S5). ^1H NMR ($CDCl_3$, 399.78 MHz): δ = 0.28 (s, 9H, CH_3), 7.26–7.30 (m, 2H, CH), 7.43–7.47 (m, 4H, CH), 7.51–7.53 (m, 2H, CH), 7.65–7.67 (m, 4H, CH), 8.06–8.08 (m, 2H, CH), 15.51 (s, 1H, NH) (SI, Figure S6). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 0.06 (CH_3), 94.8 (Csp), 105.5 (Csp), 118.8 (CH), 122.0 (C), 125.3 (CH), 127.7 (CH), 129.4 (CH), 132.1 (CH), 137.5 (C), 140.4 (C), 147.7 (C) (SI, Figure S7). UV-VIS λmax, nm (Irel, %): 252 (6671), 372 (11396). HRMS ESI TOF: exact mass found 397.1842 (397.1842 calcd. for $C_{24}H_{23}N_4Si$) (SI, Figure S8).

*3.3. 3-(4-Ethynylphenyl)-1,5-diphenylformazan (***2***)*

To 300 mg (0.76 mmol) of 1,5-diphenyl-3-[4-((trimethylsilyl)ethynyl)phenyl]formazan in 20 mL of MeOH, 420 mg (3.04 mmol) of finely ground K_2CO_3 was added. The reaction mixture was stirred at room temperature for 4 h. Then, the reaction mixture was poured into 100 mL of 2M HCl, and the precipitate was filtered and washed with water. Yield: 214 mg (87%); purple–black needles; mp 205-207 °C. Rf = 0.41 (Hexane–EtOAc 10:1). IR (KBr): ν = 3278 (Csp-H), 3062, 3045, 3030 (Csp^2-H), 2096 (Csp-Csp), 1597, 1500 (Csp^2-Csp^2), 1450, 1406, 1354, 1313, 1238, 1184, 1163, 1147, 1072, 1033, 1012, 839 cm^{-1} (SI, Figure S9). ^1H NMR ($(CD_3)_2SO$, 399.78 MHz): δ = 7.32–7.36 (m, 2H, CH), 7.49–7.57 (m, 6H, CH), 7.85–7.87 (m, 2H, CH), 8.01–8.04 (m, 2H, CH), 14.42 (s, 1H, NH) (SI, Figure S10). ^{13}C NMR ($(CD_3)_2SO$, 100.5 MHz): δ = 81.6 (Csp), 83.6 (Csp), 119.1 (CH), 120.8 (C), 126.0 (CH), 127.8 (CH), 129.5 (CH), 131.9 (CH), 136.5 (C), 140.6 (C), 147.5 (C) (SI, Figure S11). UV-VIS λmax, nm (Irel, %): 252 (6671), 372 (11396). MS (EI, 70 eV), *m/z* (Irel, %): 324 $[M^+]$ (100), 247 (4), 219 (41), 92 (31), (SI, Figure S12). HRMS ESI TOF: exact mass found 323.1277 (exact mass calculated for $C_{21}H_{14}N_4$ 323.1291) (SI, Figure S13).

Crystal data for $C_{21}H_{16}N_4$ (M = 324.38 g/mol): Orthorhombic, space group Pbca, a = 7.89300(10) Å, b = 18.6508(3) Å, c = 22.6827(3) Å, α = 90°, β = 90°, γ = 90°, V = 3339.14(8) $Å^3$, Z = 8, T = 120 K, μ = 6.21 cm^{-1}, Dcalc. = 1.290 Mg/m^3. In total, 24,973 reflections were measured, 3221 of which were unique and used in all calculations. The final R_1 was 0.0342, and the wR_2 was 0.0913 (all data) (SI, Tables S1–S7). CCDC 2,410,636 contains the supplementary crystallographic data for this paper. These data can

be obtained free of charge at http://www.ccdc.cam.ac.uk/or (accessed on 29 November 2021) from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Supplementary Materials: Figure S1: IR spectrum 1-phenyl-2-(4-((trimethylsilyl)ethynyl)benzylidene) hydrazine; Figure S2: ^{1}H NMR 1-phenyl-2-(4-((trimethylsilyl)ethynyl)benzylidene)hydrazine; Figure S3: ^{13}C NMR spectrum 1-phenyl-2-(4-((trimethylsilyl)ethynyl)benzylidene)hydrazine; Figure S4: HRMS 1-phenyl-2-(4-((trimethylsilyl)ethynyl)benzylidene)hydrazine; Figure S5: IR spectrum 1,5-diphenyl-3-(4-((trimethylsilyl)ethynyl)phenyl)formazan; Figure S6: ^{1}H NMR 1,5-diphenyl-3-(4-((trimethylsilyl) ethynyl)phenyl)formazan; Figure S7: ^{13}C NMR 1,5-diphenyl-3-(4-((trimethylsilyl)ethynyl)phenyl) formazan; Figure S8: HRMS 1,5-diphenyl-3-(4-((trimethylsilyl)ethynyl)phenyl)formazan; Figure S9: IR spectrum 3-(4-ethynylphenyl)-1,5-diphenylformazan; Figure S10: ^{1}H NMR 3-(4-ethynylphenyl)-1,5-diphenylformazan; Figure S11: ^{13}C NMR 3-(4-ethynylphenyl)-1,5-diphenylformazan; Figure S12: MS 3-(4-ethynylphenyl)-1,5-diphenylformazan; Figure S13: HRMS 3-(4-ethynylphenyl)-1,5-diphenylformazan; Figure S14: TLC (Hexane–EtOAc 10:1); (12–left, 2-right); Table S1: Crystal data and structure refinement for **2**; Table S2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor; Table S3: Bond lengths [Å] and angles [°] for **2**; Table S4: Anisotropic displacement parameters (Å$^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$; Table S5: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters (Å$^2 \times 10^3$) for **2**; Table S6: Torsion angles [°] for **2**; Table S7: Hydrogen bonds for **KV-F1** [Å and °].

Author Contributions: Conceptualization, V.V.K.; methodology, V.V.K. and D.N.K.; software, I.V.S. and D.N.K.; validation, V.V.K. and D.N.K.; formal analysis, D.N.K. and I.V.S.; investigation, I.A.L. and E.S.S.; resources, I.A.L. and E.S.S.; data curation, V.V.K.; writing—original draft preparation, V.V.K. and D.N.K.; writing—review and editing, V.V.K. and D.N.K.; supervision, V.V.K.; project administration, V.V.K.; funding acquisition, V.V.K., D.N.K., I.A.L. and E.S.S. All authors have read and agreed to the published version of the manuscript.

Funding: This publication was financially supported by the Russian Ministry of Education and Science (project no. FZEN-2023-0006).

Data Availability Statement: Data available from the corresponding authors upon reasonable request.

Acknowledgments: The HRMS study was accomplished with the use of scientific equipment of the Collective Employment Centre "Ecoanalytical Centre", Kuban State University (A. Z. Temerdashev).

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Sigeikin, G.I.; Lipunova, G.N.; Pervova, I.G. Formazans and their metal complexes. *Russ. Chem. Rev.* **2006**, *75*, 885–900. [CrossRef]
2. Lipunova, G.N.; Fedorchenko, T.G.; Chupakhin, O.N. New Aspects of the Chemistry of Formazans. *Russ. J. Gen. Chem.* **2019**, *89*, 1225–1245. [CrossRef]
3. Gilroy, J.B.; Otten, E. Formazanate coordination compounds: Synthesis, reactivity, and applications. *Chem. Soc. Rev.* **2020**, *49*, 85–113. [CrossRef] [PubMed]
4. Singh, N.; Sohal, H.S.; Verma, M.; Sharma, R.; Kaur, M. Synthesis and bio-activity of complex azo compounds: A review on formazans and its complexes. *Main Group Chem.* **2024**, *23*, 41–72. [CrossRef]
5. Shawali, A.S.; Samy, N.A. Functionalized formazans: A review on recent progress in their pharmacological activities. *J. Adv. Res.* **2015**, *6*, 241–254. [CrossRef]
6. Xu, Z.; Sung, Y.-S.; Tomat, E. Design of Tetrazolium Cations for the Release of Antiproliferative Formazan Chelators in Mammalian Cells. *J. Am. Chem. Soc.* **2023**, *145*, 15197–15206. [CrossRef]

7. Ghasemi, M.; Turnbull, T.; Sebastian, S.; Kempson, I. The MTT Assay: Utility, Limitations, Pitfalls, and Interpretation in Bulk and Single-Cell Analysis. *Int. J. Mol. Sci.* **2021**, *22*, 12827. [CrossRef]
8. Stockert, J.C.; Horobin, R.W.; Colombo, L.L.; Blázquez-Castro, A. Tetrazolium salts and formazan products in Cell Biology: Viability assessment, fluorescence imaging, and labeling perspectives. *Acta Histochem.* **2018**, *120*, 159–167. [CrossRef]
9. Grela, E.; Kozłowska, J.; Grabowiecka, A. Current methodology of MTT assay in bacteria—A review. *Acta Histochem.* **2018**, *120*, 303–311. [CrossRef]
10. Gavazov, K.B.; Dimitrov, A.N.; Lekova, V.D. The use of tetrazolium salts in inorganic analysis. *Russ. Chem. Rev.* **2007**, *76*, 169–179. [CrossRef]
11. Teslenko, F.E.; Fershtat, L.L. Unlocking Kuhn Verdazyls: New Synthetic Approach and Useful Mechanistic Insights. *Int. J. Mol. Sci.* **2023**, *24*, 2693. [CrossRef]
12. Lipunova, G.N.; Fedorchenko, T.G.; Chupakhin, O.N. Verdazyls: Synthesis, properties, application. *Russ. Chem. Rev.* **2013**, *82*, 701–734. [CrossRef]
13. Lipunova, G.N.; Fedorchenko, T.G.; Tsmokalyuk, A.N.; Chupakhin, O.N. Advances in verdazyl chemistry. *Russ. Chem. Bull.* **2020**, *69*, 1203–1222. [CrossRef]
14. Lipunova, G.N.; Fedorchenko, T.G.; Chupakhin, O.N. Verdazyls in Coordination Chemistry. *Russ. J. Coord. Chem.* **2022**, *48*, 397–411. [CrossRef]
15. Stepanov, B.I.; Avramenko, G.V. Boron—Nitrogen compounds I. Reactions of triarylformazans with diboron tetraacetate. Synthesis of boratetrazines. *J. Gen. Chem. (USSR)* **1980**, *50*, 292–295.
16. Gilroy, J.B.; Ferguson, M.J.; McDonald, R.; Patrick, B.O.; Hicks, R.G. Formazans as β-diketiminate analogues. Structural characterization of boratatetrazines and their reduction to borataverdazyl radical anions. *Chem. Commun.* **2007**, *2*, 126–128. [CrossRef]
17. Barbon, S.M.; Price, J.T.; Reinkeluers, P.A.; Gilroy, J.B. Substituent-dependent optical and electrochemical properties of triarylformazanate boron difluoride complexes. *Inorg. Chem.* **2014**, *53*, 10585–10593. [CrossRef]
18. Tikhonov, S.A.; Sidorin, A.E.; Samoilov, I.S.; Aleksandr, V.; Borisenko, A.V.; Vovna, V.I. Photoelectron spectra and electronic structure of boron diacetate formazanates. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2020**, *238*, 118441. [CrossRef]
19. Buguis, F.L.; Hsu, N.; Sung, Y.; Sirohey, S.A.; Adam, M.C.; Goncharova, L.V.; Gilroy, J.B. Dyads and Triads of Boron Difluoride Formazanate and Boron Difluoride Dipyrromethene Dyes. *Chem. A Eur. J.* **2023**, *29*, e202302548. [CrossRef]
20. Lupanova, I.A.; Konshina, D.N.; Elkov, N.A.; Konshin, V.V. 2-(4-(Dimethylamino)phenyl)-3,3-difluoro-4,6-diphenyl-3,4-dihydro-1,2,4,5,3-tetrazaborinin-2-ium-3-ide. *Molbank* **2022**, *2022*, M1312. [CrossRef]
21. Yang, S.; Lu, K.; Xiao, H. Advancements in boron difluoride formazanate dyes for biological imaging. *Curr. Opin. Chem. Biol.* **2024**, *81*, 102473. [CrossRef] [PubMed]
22. Buzykin, B.I. Formazans in the synthesis of heterocycles I. Synthesis of azoles (Review). *Chem. Heterocycl. Comp.* **2010**, *46*, 379–408. [CrossRef]
23. Buzykin, B.I. Formazans in the synthesis of heterocycles. II. Synthesis of azines (Review). *Chem. Heterocycl. Comp.* **2010**, *46*, 1043–1062. [CrossRef]
24. Dulog, L.; Breitenbucher, J. Darstellung eines (Diphenylverdazylylphenyl) propargylethers. *Liebigs Ann. Chem.* **1993**, *1993*, 201–202. [CrossRef]
25. Lupanova, I.A.; Konshina, D.N.; Konshin, V.V. Clickable ionophores for the preparation of solid materials. *AIP Conf. Proc.* **2019**, *2063*, 040036. [CrossRef]
26. Konshina, D.N.; Lupanova, I.A.; Chuprynina, D.A.; Konshin, V.V. Click functionalization in the synthesis of sorption materials. Communication I. Preparation and sorption characteristics of silicagel with immobilized formazan with regard to Pd(II) and Cu(II). *Sorbtsionnye I Khromatograficheskie Protsessy* **2018**, *18*, 568–578. [CrossRef]
27. Votkina, D.E.; Petunin, P.V.; Zhivetyeva, S.I.; Bagryanskaya, I.Y.; Uvarov, M.N.; Kazantsev, M.S.; Trusova, M.E.; Tretyakov, E.V.; Postnikov, P.S. Preparation of Multi-spin Systems: A Case Study of Tolane-bridged Verdazyl-based Hetero-diradicals. *Eur. J. Org. Chem.* **2020**, *2020*, 1996–2004. [CrossRef]
28. Magnan, F.; Dhindsa, J.S.; Anghel, M.; Bazylewski, P.; Fanchini, G.; Gilroy, J.B. A divergent strategy for the synthesis of redox-active verdazyl radical polymers. *Polym. Chem.* **2021**, *12*, 2786–2797. [CrossRef]
29. Barbon, S.M.; Gilroy, J.B. Boron difluoride formazanate copolymers with 9,9-di-n-hexylfluorene prepared by copper-catalyzed alkyne–azide cycloaddition chemistry. *Polym. Chem.* **2016**, *7*, 3589–3598. [CrossRef]
30. Barbon, S.M.; Novoa, S.; Bender, D.; Groom, H.; Luyt, L.G.; Gilroy, J.B. Copper-assisted azide–alkyne cycloaddition chemistry as a tool for the production of emissive boron difluoride 3-cyanoformazanates. *Org. Chem. Front.* **2017**, *4*, 178–190. [CrossRef]
31. Thor, S.; Krause, N. Improved Procedures for the Palladium-Catalyzed Coupling of Terminal Alkynes with Aryl Bromides (Sonogashira Coupling). *J. Org. Chem.* **1998**, *63*, 8551–8553. [CrossRef]

32. Sheldrick, G.M. SADABS v2008/4, Bruker Area Detector Absorption Correction Program. 2008. Available online: https://www.scienceopen.com/book?vid=5cab3651-c60c-4e6d-89cc-c55396e9e2dc (accessed on 9 February 2025).
33. Sheldrick, G.M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.