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Short Note

3-Phenyl-4-(prop-2-en-1-yl)-5-[(prop-2-en-1-yl)sulfanyl]-4*H*-1,2,4-triazole

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Abstract: 1,2,4-Triazoles appear to be attractive substances due to their wide range of applications. Previously 3-phenyl-4-(prop-2-en-1-yl)-5-[(prop-2-en-1-yl)sulfanyl]-4H-1,2,4-triazole (*Atr*) has proven to be an effective precursor for us to prepare Cu(I)-π,σ-coordination compounds with nonlinear optical and magnetic properties. In this study, we present the structural characterization of Atr by a single-crystal X-ray diffraction method. The crystals are monoclinic, Sp.gr. $P2_1$, Z = 2, unit cell dimensions: a = 5.6967(3), b = 7.8045(3), c = 14.9327(7) Å, β = 91.113(4)°, V = 663.78(5) Å^3 at 150 K. To analyze the intermolecular interactions in the crystal structure of Atr, a DFT computational study was also performed.

Keywords: 1,2,4-triazole; allyl derivative; crystal structure; intermolecular interaction; DFT calculation

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1. Introduction

Chemists are interested in 1,2,4-triazole derivatives mainly because of their wide range of pharmacological activities, such as antifungal, herbicidal, antiviral and anticancer activities, as well as catalase inhibitors. Some drugs that are clinically used for the treatment of various diseases are based on them [1–8]. Commercial fungicides also contain triazoles [9]. Among azoles, triazoles are the most stable compounds and are becoming increasingly attractive as organic ligands for the crystal engineering of transition metal organometallic compounds with catalytic, luminescent, biochemical, spin crossover activities, etc. [10–17]. The versatile possibility of easy functionalization of triazole molecules is also favorable. Among allyl derivatives, the 3-phenyl-4-allyl-5-allylsulfanyl 4*H*-1,2,4-triazole (*Atr*) was recently shown to be an effective precursor for the preparation of a Cu(I)-π,σ-coordination compound with nonlinear optical and magnetic properties [18]. Due to the π,σ-coordination to copper(I) ions via the η_2-allyl group and the two heterocyclic N atoms, *Atr* molecules form compounds based on dimeric building blocks $\{Cu_2(Atr)_2\}$ that are stable both in crystalline form and in solution [18,19]. Such stability in solution (usually in ethanol or acetonitrile) is not characteristic of Cu(I) π-complexes with other allylazoles, such as 1,2,3-triazoles, tetrazoles, 1,3,4-thiadiazoles, and 1,3,4-oxadiazoles [20–23]. Despite the fact that all investigated crystalline copper coordination compounds with *Atr* were studied by the single-crystal X-ray diffraction method, while *Atr* itself was characterized only by spectroscopic techniques [19], in the present work, we focused on the structural characterization of 3-phenyl-4-(prop-2-en-1-yl)-5-[(prop-2-en-1-yl)sulfanyl]-4*H*-1,2,4-triazole (*Atr*) (Figure 1) by the diffraction technique, accompanied by an energy framework computational study.

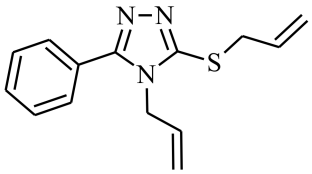

Figure 1. Chemical structure for the title compound (*Atr*).

2. Results and Discussion

Atr crystallizes in the acentric space group $P2_1$ with one molecule in the asymmetric unit (Figure 2, Table 1). The triazole ring and conjugated phenyl ring are twisted relative to each other by 43.2(1)°. All C atoms of the allylsulfanyl group are disordered over two sites (the site-occupation factors are 0.580(11) for A and 0.420(11) for B). The second allyl (N-bound) group tends to orthogonally location to the heterocyclic ring, and the angle between this allyl group and triazole plane is 76.05(8)°. A similar orientation of the N-bound allyl group was observed in all earlier studied copper(I) π,σ-coordination compounds with *Atr* [18,19]. It is worth noting that, because of the electron-withdrawing effect of the triazole system on the N-bound allyl group, the π-coordination of this allyl substituent with Cu(I) was not observed. Instead, an effective interaction of Cu^+ with the C=C bond of allylsulfanyl group was observed in the crystal structures of the corresponding coordination compounds as well as in its acetonitrile solutions. The allylsulfanyl group over part A has an anticlinal conformation relative to the S1—C6 bond (C1—S1—C6A—C7A, 129.9(6)°), while over part B, it has an antiperiplanar conformation (C1—S1—C6B—C7B, –164.7(8)°).

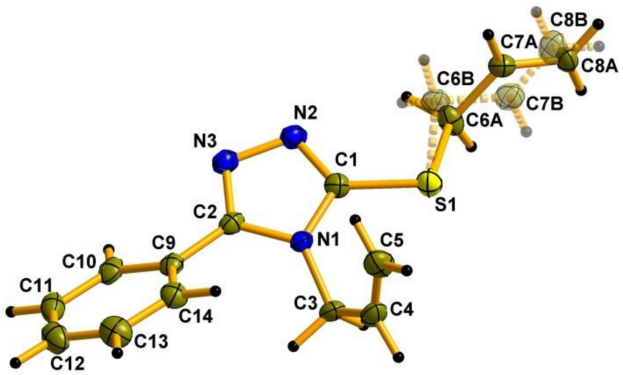

Figure 2. The independent part in *Atr* crystal structure. One of the two disordered positions of the allyl group, i.e., with the lower site-occupancy factor, is shown in semi-transparent mode. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Selected geometric parameters (Å, °) of *Atr*.

Bond	*d*, Å	Angle	ω, °
C1—N2	1.310(3)	N1—C3—C4	114.9(2)
N2—N3	1.401(3)	C3—C4—C5	125.7(2)
C1—N1	1.370(3)	C1—S1—C6A	104.0(2)
C4—C5	1.304(3)	S1—C6A—C7A	110.6(4)
C7A—C8A	1.339(11)	C6A—C7A—C8A	122.0(9)
S1—C1	1.744(2)	C6B—C7B—C8B	122.6(14)

According to the energy framework calculation results, the most prominent intermolecular interactions, which cover a total energy of −47.0 kJ/mol for model A and −48.8 kJ/mol for model B, mainly correspond to a C5—H5A···π(Ph) (2.69 Å) interaction with two neighboring molecules (Figure 3). The energy value of interaction with the next pair of molecules cover a total energy of −25.9 kJ/mol (Model A) and −20.7 kJ/mol

(Model B) and corresponds to hydrogen bonding (C8A—H8AA···N3 (2.62 Å) and C7B—H7B···N2 (2.60 Å)) between the allylsulfanyl group and triazole N atoms. The other pairs of molecules form the C—H···π interactions with neighboring phenyl rings and phenyl ring and C=C bonds of N-allyl group. The energy value of these interactions includes the total energy of −15.5 kJ/mol for model A and −15.4 kJ/mol for model B. All mentioned interactions link the molecules into a three-dimensional network. The total energy of all the interactions is −124.7 kJ/mol in A and −121.3 kJ/mol in B.

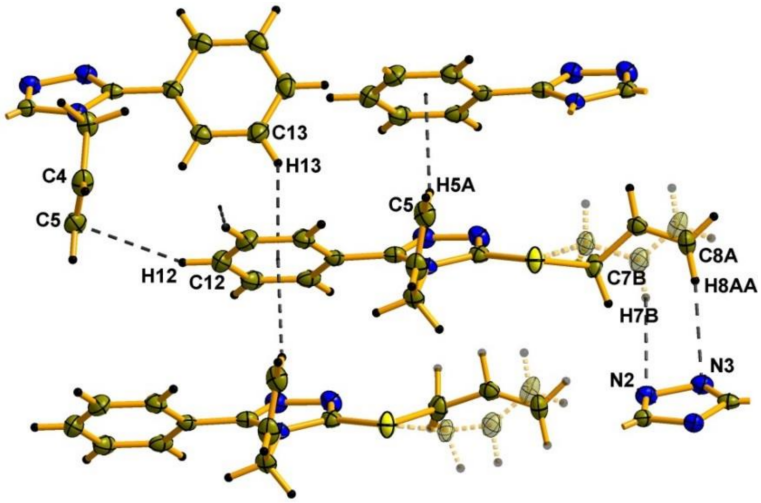

Figure 3. The weak interactions between the molecules in *Atr* crystal structure.

3. Materials and Methods

3.1. Materials and Instrumentation

Unless mentioned otherwise, all chemicals were obtained from commercial sources (Sigma Aldrich, St. Louis, MO, USA) and used without further purification. The NMR experiments: ^{1}H NMR (500 MHz), ^{13}C{^{1}H} NMR (125 MHz) for 3-phenyl-4-(prop-2-en-1-yl)-5-[(prop-2-en-1-yl)sulfanyl]−4*H*-1,2,4-triazole (*Atr*) were recorded on a Bruker Avance 500 MHz NMR spectrometer (Bruker, Bremen, Germany). The chemical shifts are reported in ppm relative to the residual peak of the deuterated CD_3CN for the ^{1}H and ^{13}C{^{1}H} NMR spectra. The infrared (IR) spectrum was recorded on FT-IR Spectrum BX-II (Perkin Elmer, Waltham, MA, USA) in nujol mulls. Diffraction data for *Atr* single crystal were collected on an Agilent Gemini A four-circle diffractometer (Yarnton, Oxfordshire, OX5 1QU, UK) with Atlas CCD detector.

3.2. Synthesis of Atr

3-Phenyl-4-(prop-2-en-1-yl)-5-[(prop-2-en-1-yl)sulfanyl]-4*H*-1,2,4-triazole (*Atr*) was obtained in several steps in accordance with the reported method [18,19]. Benzhydrazide was converted into N-allyl-2-benzoylhydrazinecarbothioamide by the reaction with allyl isothiocyanate, followed by the cyclization of the obtained carbothioamide with aqueous sodium hydroxide solution into 3-phenyl-4-(prop-2-en-1-yl)-1*H*-1,2,4-triazole-5-thiol. Triazole then readily reacted with allyl chloride in the presence of KOH in ethanol solution, yielding the corresponding *Atr*. M.p. 49 °C. ^{1}H NMR (CD_3CN, 500 MHz) δ_H 7.68–7.58 (2H, m), 7.58–7.47 (3H, m), 6.05–5.86 (2H, m), 5.32–5.16 (2H, m), 5.11 (1H, d, J = 10.1 Hz), 4.85 (1H, d, J = 17.2 Hz), 4.65–4.54 (2H, m), 3.83 (2H, d, J = 7.1 Hz). ^{13}C NMR (CD_3CN, 126 MHz) δ_C 155.8, 150.8, 133.4, 132.4, 130.2, 128.9, 128.5, 128.4, 127.4, 118.1, 117.4, 116.9, 46.6, 36.2. IR (Nujol, cm^{-1}): 411 w, 432 w, 475 w, 495 w, 530 m, 563 m, 587 m, 603 m, 700 vs, 770 vs, 855 w, 877 m, 920 s, 936 s, 979 m, 996 m, 1024 m, 1075 m, 1108 w, 1137 w, 1160 w, 1201 s, 1232 m, 1257 w, 1285 w, 1298 w, 1324 m, 1353 m, 1371 m, 1387 m, 1424 vs, 1438 m, 1460 vs, 1475 s, 1525 w, 1580 m, 1605 m, 1635 m, 1651 m, 1702 m, 1773 vw, 1821 vw, 1847 w, 1897 w, 1960 w, 1980 vw, 2024 vw, 2341 w, 2362 w, 2548 vw, 2612 vw, 2711 vw, 2853 w, 2932 m, 2976 m, 3010 m, 3082 m.

3.3. Single Crystal X-ray Diffraction Studies

High-quality single crystals of *Atr* were obtained by slow evaporation of their ethanol solutions. The collected diffraction data were processed with the CrysAlis PRO program (Version 1.171.41.104a, Rigaku OD, 2021) [24]. The structure was determined by ShelXT and refined by least squares method on F^2 by ShelXL software with the following graphical user interface of OLEX^2 [25–27]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters. The figures were prepared using DIAMOND 3.1 software (Crystal Impact GbR, Bonn, Germany).

Crystal data for *Atr* ($C_{14}H_{15}N_3S$, M = 257.35 g/mol): monoclinic crystal system, space group $P2_1$, Z = 2, unit cell dimensions: a = 5.6967(3), b = 7.8045(3), c = 14.9327(7) Å, β = 91.113(4)°, V = 663.78(5) Å^3 at 150 K; $\rho_{calc.}$ = 1.288 g/cm^3, $R[F^2 > 2\sigma(F^2)]$ = 0.0312 for 2799 reflections and $wR(F_2)$ = 0.0707 for all 3012 reflections. Data were deposited at the Cambridge Crystallographic Data Centre as CCDC 2176148, which 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/structures/.

3.4. Computational Study

Energy framework calculations were performed on the DFT/B3LYP/6-31G(d, p) level using the CrystalExplorer 17.5 software (University of Western Australia, Perth, Australia). All the calculations were provided for clusters of molecules within a radius of 3.8 Å, which were generated around a single fragment.

Supplementary Materials: The following supporting information can be downloaded online. This information includes CIF-file of C14H15N3S (Atr) and corresponding checkCIF/PLATON report for it.

Author Contributions: Y.I.S. conceptualization, investigation, methodology; software, writing—original draft; E.A.G. software, investigation; A.M.F. investigation; M.G.M. software, investigation. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The X-ray data were deposited at CCDC as stated above.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ji Ram, V.; Sethi, A.; Nath, M.; Pratap, R. Five-membered heterocycles. In *The Chemistry of Heterocycles*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 149–478.
2. Abdelli, A.; Azzouni, S.; Plais, R.; Gaucher, A.; Efrit, M.L.; Prim, D. Recent advances in the chemistry of 1,2,4-triazoles: Synthesis, reactivity and biological activities. *Tetrahedron Lett.* **2021**, *86*, 153518. [CrossRef]
3. Aggarwal, R.; Sumran, G. An insight on medicinal attributes of 1,2,4-triazoles. *Eur. J. Med. Chem.* **2020**, *205*, 112652. [CrossRef] [PubMed]
4. Kaur, R.; Ranjan Dwivedi, A.; Kumar, B.; Kumar, V. Recent developments on 1,2,4-triazole nucleus in anticancer compounds: A Review. *Anticancer Agents Med. Chem.* **2016**, *16*, 465–489. [CrossRef] [PubMed]
5. Aggarwal, R.; Hooda, M.; Kumar, P.; Sumran, G. Vision on synthetic and medicinal facets of 1,2,4-triazolo[3,4-b][1,3,4]thiadiazine scaffold. *Top. Curr. Chem.* **2022**, *380*, 10. [CrossRef]
6. Guo, H.-Y.; Chen, Z.-A.; Shen, Q.-K.; Quan, Z.-S. Application of triazoles in the structural modification of natural products. *J. Enzym. Inhib. Med. Chem.* **2021**, *36*, 1115–1144. [CrossRef]
7. Tratrat, C. 1,2,4-Triazole: A privileged scaffold for the development of potent antifungal agents—A brief review. *Curr. Top. Med. Chem.* **2020**, *20*, 2235–2258. [CrossRef]
8. Gupta, D.; Jain, D. Synthesis, antifungal and antibacterial activity of novel 1,2,4-triazole derivatives. *J. Adv. Pharm. Technol. Res.* **2015**, *6*, 141. [CrossRef]

9. Russell, P.E. A century of fungicide evolution. *J. Agric. Sci.* **2005**, *143*, 11–25. [CrossRef]
10. Aromí, G.; Barrios, L.A.; Roubeau, O.; Gamez, P. Triazoles and tetrazoles: Prime ligands to generate remarkable coordination materials. *Coord. Chem. Rev.* **2011**, *255*, 485–546. [CrossRef]
11. Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M. Metal azolate frameworks: From crystal engineering to functional materials. *Chem. Rev.* **2012**, *112*, 1001–1033. [CrossRef]
12. Roubeau, O. Triazole-based one-dimensional spin-crossover coordination polymers. *Chem.-A Eur. J.* **2012**, *18*, 15230–15244. [CrossRef]
13. Yang, L.; Shen, Y.; Chen, Y.; Pan, X.; Wang, X.; Wang, X. A Novel octamolybdate-based metal-organic complex constructed from a bis(tetrazole)-functionalized thioether ligand and an anderson-type polyoxometalate. *Inorg. Chem. Commun.* **2019**, *108*, 107493. [CrossRef]
14. Vinogradova, K.A.; Pishchur, D.P.; Komarov, V.Y.; Lavrenova, L.G.; Bushuev, M.B. Cooperative spin transition in a 1*D*-polymeric complex [Fe(4-Ethyl-1,2,4-Triazole$_{)3}$]SiF_6·nH_2O. *Inorg. Chim. Acta* **2020**, *506*, 119560. [CrossRef]
15. Li, J.; Ren, G.-Y.; Zhang, Y.; Yang, M.-Y.; Ma, H.-X. Two Cu(II) complexes of 1,2,4-triazole fungicides with enhanced antifungal activities. *Polyhedron* **2019**, *157*, 163–169. [CrossRef]
16. Nguyen, V.H.; Nguyen, H.H.; Do, H.H. 1,2,4-Triazole-derived N-heterocyclic carbene complexes of platinum(II) as catalysts for hydroamination reactions and active anticancer agents. *Inorg. Chem. Commun.* **2020**, *121*, 108173. [CrossRef]
17. Ouellette, W.; Jones, S.; Zubieta, J. Solid state coordination chemistry of metal-1,2,4-triazolates and the related metal-4-pyridyltetrazolates. *CrystEngComm* **2011**, *13*, 4457. [CrossRef]
18. Hordiichuk, O.R.; Slyvka, Y.I.; Kinzhybalo, V.V.; Goreshnik, E.A.; Bednarchuk, T.J.; Bednarchuk, O.; Jedryka, J.; Kityk, I.; Mys'kiv, M.G. Construction of heterometallic and mixed-valence copper(I/II) chloride π-complexes with 1,2,4-triazole allyl-derivative. *Inorg. Chim. Acta* **2019**, *495*, 119012. [CrossRef]
19. Hordiichuk, O.R.; Kinzhybalo, V.V.; Goreshnik, E.A.; Slyvka, Y.I.; Krawczyk, M.S.; Mys'kiv, M.G. Influence of apical ligands on Cu–(C=C) interaction in copper(I) halides (Cl^-, Br^-, I^-) π-complexes with an 1,2,4-triazole allyl-derivative: Syntheses, crystal structures and NMR spectroscopy. *J. Organomet. Chem.* **2017**, *838*. [CrossRef]
20. Slyvka, Y.; Goreshnik, E.; Veryasov, G.; Morozov, D.; Fedorchuk, A.A.; Pokhodylo, N.; Kityk, I.; Mys'kiv, M. The novel copper(I) π,σ-complexes with 1-(aryl)-5-(allylthio)-1*H*-tetrazoles: Synthesis, structure characterization, DFT-calculation and third-order nonlinear optics. *J. Coord. Chem.* **2019**, *72*, 1049–1063. [CrossRef]
21. Pavlyuk, O.V.; Slyvka, Y.I.; Goreshnik, E.A.; Mys'kiv, M.G. 6-Amino-3-(prop-2-en-1-yl)-9*H*-purin-3-ium tetracopper(I) hexabromide: Synthesis and X-ray structure determination. *Molbank* **2022**, *2022*, M1401. [CrossRef]
22. Slyvka, Y.; Kinzhybalo, V.; Shyyka, O.; Mys'kiv, M. Synthesis, structure and computational study of 5-[(prop-2-en-1-yl)sulfanyl]-1,3,4-thiadiazol-2-amine (*Pesta*) and its heterometallic π,σ-complex [Cu_2FeCl_2(*Pesta*)$_4$][$FeCl_4$]. *Acta Crystallogr. Sect. C Struct. Chem.* **2021**, *77*, 249–256. [CrossRef]
23. Slyvka, Y.; Goreshnik, E.; Veryasov, G.; Morozov, D.; Luk'yanov, M.; Mys'kiv, M. The first copper(I)-olefin complexes bearing a 1,3,4-oxadiazole core: Alternating-current electrochemical crystallization, X-ray experiment and DFT study. *Polyhedron* **2017**, *133*, 319–326. [CrossRef]
24. Rigaku Oxford Diffraction. Rigaku CrysAlisPro Software System, Version 1.171.41.104a. 2021. Available online: http://www.rigaku.com (accessed on 1 September 2021).
25. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8. [CrossRef]
26. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8. [CrossRef] [PubMed]
27. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341. [CrossRef]