One-pot microwave-assisted synthesis of 2,5-bis(pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazoles from pyrazole-4-carbaldehydes and dithiooxamide

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Abstract
An efficient one-pot method for the synthesis of previously unknown of 2,5-bis(pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazoles has been developed. The method comprises the microwave-assisted reaction of dithiooxamide with pyrazole-4-carbaldehydes followed by oxidation of the initially formed 2,5-dihydro[1,3]thiazolo[5,4-*d*][1,3]thiazoles with selenium dioxide. 2,5-Bis(pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazoles were characterized by ^{1}H, ^{13}C and ^{15}N NMR, IR spectroscopy and X-ray diffraction data.

Keywords: Microwave activated reaction, pyrazolecarbaldehydes, thiazolo[5,4-*d*]thiazoles, X-ray diffraction

Introduction

Thiazolo[5,4-*d*]thiazoles represent an important class of bicyclic aromatic structures that have attractive properties for application in electronics,[1-9] optoelectronics,[10,11] and as ligands in coordination chemistry[10,12] etc. Many fused thiazoles are also biologically active and constitute an essential motif of pharmacologically active connections.[4,13-16]

Among 2,5-bisaromatic and 2,5-bisheteroaromatic derivatives of thiazolo[5,4-*d*]thiazole, 2,5-bispyrazolylthiazolo[5,4-*d*]thiazoles are poorly understood. Only one synthesis has been reported[17] of the linear thermally stable 2,5-bis[4-(1*H*-pyrazol-4-yl)phenyl][1,3]thiazolo[5,4-*d*][1,3]thiazole, which bears pyrazole units at the 4 position of the phenyl rings which have no significant effect on properties of the thiazolothiazole ring.

Pyrazole and its derivatives are attracting considerable interest because of wide spectrum of their pharmacological activity.[18-23] Furthermore, pyrazoles are used as agrochemicals, and applied

in modern practical disinsection.[24-26] Pyrazoles are used in supramolecular and polymer chemistry,[27] as cosmetic colorings and UV stabilizers.[19,28] They are also used to design of complexes with unusual magnetic properties.[29]

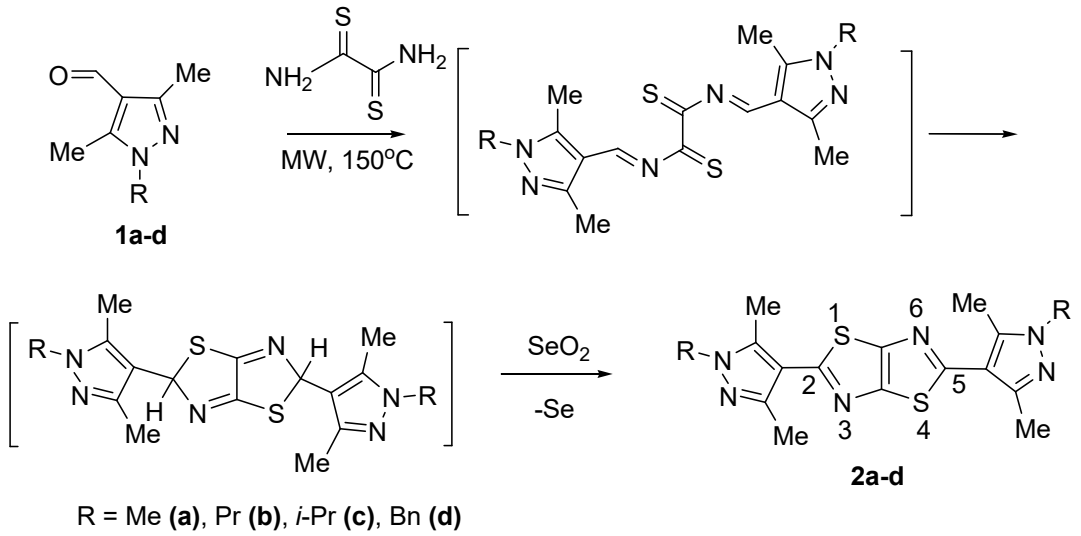
Synthetic approaches to 2,5-disubstituted thiazolo[5,4-*d*]thiazoles are limited in number, laborious and require harsh reaction conditions. A popular method for the preparation of diaryl-substituted thiazolo[5,4-*d*]thiazole, reported for the first time,[30] is based on the condensation of dithiooxamide with excess aromatic aldehydes (10-12-fold molar excess), which is used for oxidation of the initially formed products. This reaction is carried out in diverse solvents,[10,31-34] or without solvent.[6,15,16,18] However, the harsh reaction conditions and duration of the process (24 h) lead to resinification and formation of the side products. The developed alternative approaches to the synthesis of diarylthiazolo[5,4-*d*]thiazoles such as treatment of 2,5-bis(acetylamino)thiazole with sodium thiocyanate in the presence of bromine followed by thermal cyclization,[35] acid-catalyzed reaction of 5-amino-2-aryl-4-mercaptothiazole with orthoether[36] and others[1] are of limited utility.

In 2014, a method for the preparation of 2,5-disubstituted [1,3]thiazolo[5,4-*d*][1,3]-thiazoles was elaborated (yields 6-81%).[37] The method comprises the interaction of a diverse range of aldehydes with dithiooxamides in nitrobenzene at 4:1 or 2:1 reagents ratio. Also, the first stage of the process involves microwave activation to obtain the intermediate nonaromatic thiazolinothiazolines. For the synthesis of the target thiazolothiazoles, oxidation of the intermediate heterocycles with chloroanil or DDQ is employed at the second stage of the process. The two-stage character of the reaction and the application the aforementioned expensive toxic oxidizing agents, hinders isolation and purification of the target thiazolothiazoles.

Results and Discussion

Recently, we developed a one-pot microwave-assisted method for the synthesis of 2,5-bisarylthiazolo[5,4-*d*]thiazoles from benzaldehydes and dithiooxamide.[38] The reaction is carried out under microwave activation at both steps (condensation of dithiooxamide with aromatic aldehydes and oxidative aromatization of intermediate 2,5-dihydrothiazolo[5,4-*d*]thiazoles with SeO_2). We have employed for the first time SeO_2 as an oxidizing agent. Unlike chloroanil and DDQ, SeO_2 in the course of the process is transformed to the low toxic elemental selenium, which is not dissolved in reaction mixtures and easily separated from reaction products.

In the present work, we have applied this method to synthesize hitherto unknown 2,5-bispyrazolyl[1,3]thiazolo[5,4-*d*][1,3]thiazoles from pyrazole-4-carbaldehydes and dithiooxamide. The interaction of pyrazole-4-carbaldehydes **1a-d** with dithiooxamide and SeO_2 was carried out at 2:1:1 reagents molar ratio in DMF solution (Scheme 1).



Scheme 1. Synthesis of 2,5-bispyrazolyl[1,3]thiazolo[5,4-*d*][1,3]thiazoles from pyrazole-4-carbaldehydes and dithiooxamide.

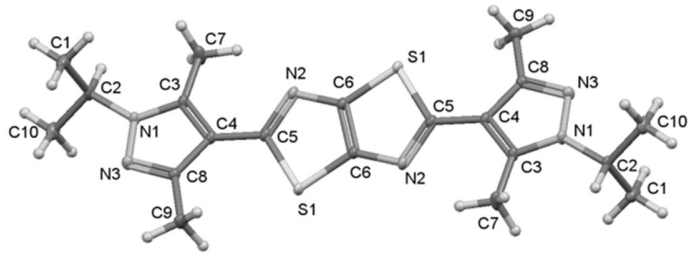
The elemental selenium, which formed during the reaction, was easily separated allowing the facile isolation of thiazolo[5,4-d]thiazoles **2a-d**. Unlike the known procedure,[37] this protocol did not require additional purification of the products on chromatographic column.

It should be noted that while diarylthiazolothiazoles can be synthesized by the reaction of the corresponding benzaldehydes with dithiooxamide without microwave irradiation, the interaction of pyrazole-4-carbaldehydes with dithiooxamide affording bispyrazolyl-thiazolo[5,4-*d*]thiazoles cannot be implemented without microwave activation. Under the conditions reported in literature[18,30,34] or upon the reagents heating at 130 °C for 3 h in DMSO, the reaction mixture darkens and resinifies, only the initial aldehyde being detected among the reaction products.

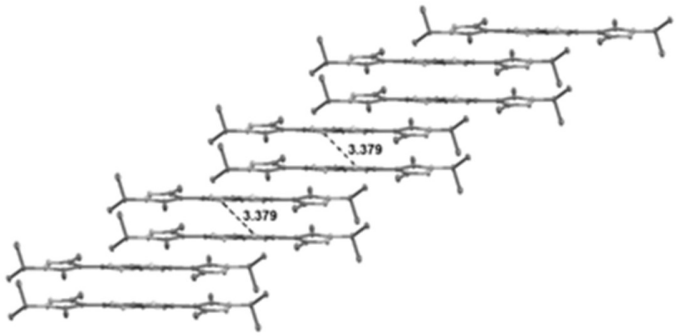
The 2,5-bispyrazolyl[1,3]thiazolo[5,4-*d*][1,3]thiazoles **2a-d** obtained are high-melting light-colored compounds, which are poorly soluble in organic solvents. The structure and composition of thiazolo[5,4-*d*]thiazoles **2a-d** have been supported by IR, ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy and elemental analysis. In the IR spectrum of compounds **2a-d**, characteristic absorption bands of the carbonyl groups of the initial aldehydes **1a-d** are absent. In the ^{1}H NMR spectra, the signals of aldehyde group protons disappear, while the proton signals of substituents in the pyrazole ring, having corresponding integral intensity, are observed. The ^{13}C NMR spectra of thiazolo[5,4-*d*]thiazoles **2a-d** show characteristic signals of the thiazolothiazole carbon atoms (147.8-148.9 ppm, C-7 and C-8) and (161.8-162.0 ppm, C-2 and C-5). In the ^{15}N NMR spectra, the signals of N-1 and N-2 atoms of the pyrazole ring are observed. The signals of the thiazole cycles have not been detected in the ^{15}N NMR spectra due to poor solubility of the products.

To investigate the molecular structure and intermolecular interactions in the solid state, X-ray structure analysis of the single crystal of compound **2c** was carried out. The single crystals of **2c**

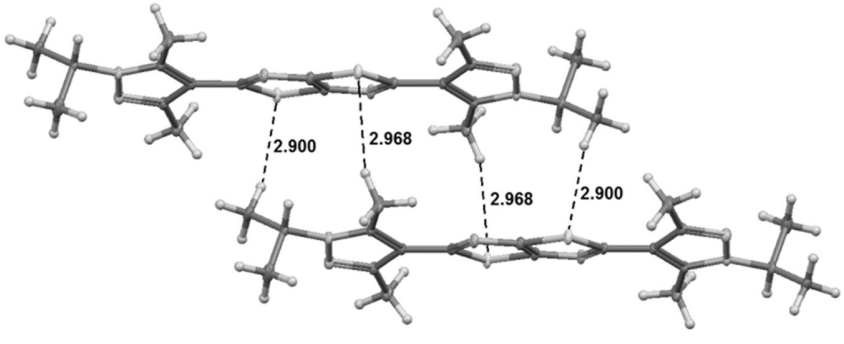
were obtained by slow evaporation from dimethylformamide. The molecular structure of thiazolothiazole **2c** is depicted in Figure 1.



(a)



(b)



(c)

Figure 1. (a) Crystal structure of 2,5-bis[3,5-dimethyl-1-(1-methylethyl)-1*H*-pyrazol-4-yl][1,3]thiazolo[5,4-*d*][1,3]thiazole (**2c**); (b) layered crystal structure of compound **2c**; (c) intermolecular interactions between two molecules of compound **2c** according to the X-ray diffraction data.

2,5-Bis[3,5-dimethyl-1-(1-methylethyl)-1*H*-pyrazol-4-yl][1,3]thiazolo[5,4-*d*][1,3]-thiazole (**2c**) has a highly symmetric structure with an inversion center at the middle point of the C(6) – C(6i) bond (Figure 1a). Compound **2c** have simple stacking structure where all molecular planes are parallel to each other. They form columnar structures with intermolecular short S···S contacts between the thiazolothiazole rings equal 3.379 Å (Figure 1b). In addition there are short C-H···S

contacts between methyl groups and sulfur atoms of neighboring molecules (Figure 1c). In contrast to pyridine or phenyl structures with thiazolo-thiazole fragment where pyridine[12] or phenyl[10,31] ring does not exceed 5.5°, angle between pyrazole and thiazolothiazole planes in compound **2c** consists 16.83°.

Conclusions

A facile and efficient one-pot method for the synthesis of 2,5-bispyrazol-4-yl-thiazolo[5,4-*d*]thiazoles has been developed. The method comprises the microwave-assisted reaction of dithiooxamide with pyrazole-4-carbaldehydes followed by oxidation of the initially formed bispyrazolothiazolinothiazolines with SeO_2. The protocol does not require the use of excess aldehyde and is less laborious compared to the known syntheses of thiazolo[5,4-*d*]thiazoles.

Experimental Section

General. The ^{1}H, ^{13}C, ^{15}N NMR spectra were recorded on Bruker DPX-400 (400.13, 100.62 and 40.55 MHz, respectively) from solutions in (DMSO-d_6) and $CDCl_3$ relative to HMDS (^{1}H, ^{13}C) and CH_3NO_2 (^{15}N). Chemical shifts are reported in ppm values (δ) and coupling constants (J) in Hz. The IR spectra were taken in KBr on a Bruker Vertex 70 instrument. The elemental analyses were obtained on a Thermo Scientific Flash 2000 CHNS analyzer. The melting points were determined on a PolyTherm A micro hot stage. Starting dithiooxamide was taken from commercial suppliers and used without further purification. Pyrazole-4-carbaldehydes **1a-d** were synthesized according to the literature.[39] Reactions were carried out in the microwave reactor Anton Paar Monowave 300 under inert atmosphere at fixed temperature (control external surface sensor) and variable power (maximum power 400 W).

General procedure for Synthesis of 2,5-bis(pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazole (2a-d). In a microwave glass vial equipped with a magnetic stirrer, the corresponding pyrazole-4-carbaldehyde (**1a-d**) (2.0 mmol), dithiooxamide (120 mg, 1.0 mmol) and DMF (2 mL) were loaded and the vial was filled with argon. The vial was closed, the reaction mixture was heated under microwave irradiation at 150 °C for 3 h, then cooled to 55 °C, and selenium dioxide (114 mg, 1.0 mmol) was added. The mixture was stirred additionally for 15-30 min at 180 °C and cooled to room temperature. Afterwards, the reaction mixture was allowed to stand overnight in the cold, methanol (4 mL) was added and the aggregated elemental selenium was separated. The crude product was filtered, washed with DMF, methanol, ether and dried under vacuum (1 mm Hg) to constant weight.

2,5-Bis(1,3,5-trimethyl-1*H*-pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazole (2a). Beige powder, yield: 152 mg (42%); mp 278-279 °C ($CHCl_3$). IR (KBr), ν, cm^{-1}: 2917, 1548, 1437, 1384, 1310,

1118, 1042, 886, 639. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ_H (ppm): 2.51 (6H, s, 2Me-3), 2.59 (6H, s, 2Me-5), 3.79 (6H, s, 2MeN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ_C (ppm): 11.4 (Me-5); 14.0 (Me-3); 113.7 (C-4 pyr), 139.2 (C-5 pyr), 146.2 (C-3 pyr), 148.9 (C-7, C-8), 161.8 (C-2, C-5). ^{15}N NMR (40.55 MHz, $CDCl_3$), δ_N (ppm): (ref. CH_3NO_2): -182.6 (N-1), -79.7 (N-2). Anal. Calcd for $C_{16}H_{18}N_6S_2$ (358.48): C, 53.61; H, 5.06; N, 23.44; S 17.89. Found: C, 53.54; H, 5.22; N, 23.46; S, 17.78%.

2,5-Bis(3,5-dimethyl-1-propyl-1*H*-pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazole (2b). Pale-yellow crystals, yield: 177 mg (43%); mp 169-171 °C (DMF). IR (KBr), ν, cm^{-1}: 2934, 2873, 1549, 1508, 1435, 1311, 1308, 1044, 1007. ^{1}H NMR (400.13 MHz, DMSO-d_6), δ_H (ppm): 0.89 (6H, t, $^{3}J_{HH}$ 6.8 Hz, 2*Me*CH_2CH_2), 1.77 (4H, sex, $^{3}J_{HH}$ 6.8 Hz, 2Me*CH*$_2$$CH_2$), 2.43 (6H, s, 2Me-3), 2.60 (6H, s, 2Me-5), 4.04 (4H, t, $^{3}J_{HH}$ 6.8 Hz, 2MeCH$_2$*CH*$_2$). ^{13}C NMR (100.62 MHz, DMSO-d_6), δ_C (ppm): 10.9 (*C*H$_3$-C^5), 10.9 (*Me*CH_2CH_2), 13.9 (Me-3), 22.8 (Me*C*H_2CH_2), 49.8 (MeCH$_2$*C*H$_2$N), 112.4 (C-4 pyr), 138.8 (C-5 pyr), 145.1 (C-3 pyr), 147.8 (C-7, C-8), 161.5 (C-2, C-5). ^{15}N NMR (40.55 MHz**,** DMSO-d_6), δ_N (ppm): (ref. CH_3NO_2): -168.1 (N-1), -77.4 (N-2). Anal. Calcd for $C_{20}H_{26}N_6S_2$ (414.59): C, 57.94; H, 6.32; N, 20.27; S 15.47. Found: C, 57.89; H, 6.35; N, 20.42; S 15.43%.

2,5-Bis[3,5-dimethyl-1-(1-methylethyl)-1*H*-pyrazol-4-yl][1,3]thiazolo[5,4-*d*][1,3]thiazole (2c). The target product **2c** was precipitated upon cooling of the reaction mixture obtained from 3,5-dimethyl-1-(1-methylethyl)-1*H*-pyrazole-4-carbaldehyde (**1c**). Colorless crystals, yield: 191 mg (46%); mp 204-205 °C ($CHCl_3$). IR (KBr), ν, cm^{-1}: 2972, 1546, 1475, 1437, 1303, 1203, 1040, 1008, 897, 871, 616. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ_H (ppm): 1.49 (12H, d, $^{3}J_{HH}$ 6.7 Hz, 2*Me*$_2$CH), 2.59 (6H, s, 2Me-3), 2.51 (6H, s, 2Me-5), 4.46 (2H, septet, $^{3}J_{HH}$ 6.7 Hz, 2C*H*Me$_2$). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ_C (ppm): 10.9 (Me-5), 14.2 (Me-3), 22.3 (*Me*$_2$CH), 49.7 (Me$_2$*C*HN), 113.4 (C-4 pyr), 137.8 (C-5 pyr), 146.1 (C-3 pyr), 148.9 (C-7, C-8), 162.0 (C-2, C-5). ^{15}N NMR (40.55 MHz**,** $CDCl_3$), δ_N (ppm): (ref. CH_3NO_2): -159.0 (N-1); -88.7 (N-2). Anal. Calcd for $C_{20}H_{26}N_6S_2$ (414.59): C, 57.94; H, 6.32; N, 20.27; S, 15.47. Found: C, 57.98; H, 6.27; N, 20.41; S, 15.34%.

2,5-Bis(3,5-dimethyl-1-benzyl-1*H*-pyrazol-4-yl)[1,3]thiazolo[5,4-*d*][1,3]thiazole (2d) Pale-yellow powder, yield: 279 mg (62%); mp 235-236 °C (DMF). IR (KBr), ν, cm^{-1}: 2951, 2916, 1548, 1507, 1488, 1433, 1312, 1044, 890, 639, 574. ^{1}H NMR (400.13 MHz, DMSO-d_6), δ_H (ppm): 2.44 (6H, s, 2Me-3), 2.55 (6H, s, 2Me-5), 5.36 (4H, s, 2N*CH*$_2$Ph), 7.18 (4H, m, H^o), 7.28 (2H, m, H^p), 7.35 (4H, m, H^m). The ^{13}C and ^{15}N were not recorded due to extremely poor solubility of the compound **2d** in most organic solvents. Anal. Calcd for $C_{28}H_{26}N_6S_2$ (510.67): C, 65.85; H, 5.13; N, 16.46; S, 12.56. Found: C, 65.58; H, 5.32; N, 16.51; S, 12.59%.

X-ray study and refinement of compound (2c). Crystal data were collected on a Bruker D8 Venture diffractometer with MoKa radiation (λ = 0.71073Å) using the φ and ω scans. The structures were solved and refined by direct methods using the SHELX programs set.[40] Data were corrected for absorption effects using the multi-scan method (SADABS). Nonhydrogen atoms were refined anisotropically using SHELX.[40]

Crystallographic data for the structure of **2c** have been deposited in the Cambridge Crystallographic Data Centre as a CIF deposition with file number CCDC-1436855. Copies of these data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk) or from http://www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Information

^{1}H-NMR, ^{13}C-NMR and X-ray data of compounds can be found in the Supplementary Material section of this article.

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