Reactions of pyrazinium salts with phenols: from σ^H-adducts to S_N^H products and transformations into benzo[*b*]furans

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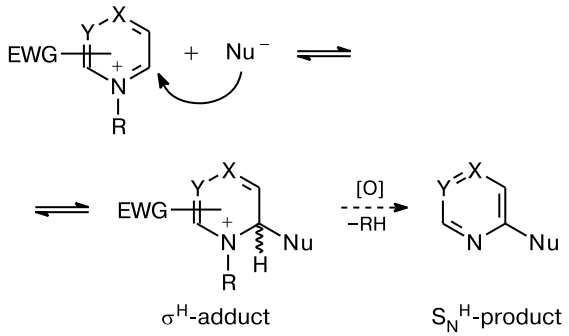
The reaction of 5-(het)aryl-2,3-dicyano-1-ethylpyrazinium salts with phenol derivatives affords relatively stable dihydropyrazines, whereas the reactions of 6-(het)aryl-1,2,5-oxadiazolo[3,4-*b*]pyrazin-4-ium protic salts, depending on the phenol structure, result in products of nucleophilic substitution of hydrogen or open-chain transformation products: benzo[*b*]furan-substituted derivatives. The crystallographic data on the spatial structure of all types of the synthesized products were obtained.

Key words: pyrazinium salts, phenols, 1,2-dihydropyrazines, σ^H-adducts, nucleophilic substitution of hydrogen (S_N^H).

Azinium salts are active heteroaromatic substrates capable of chemical modifying under relatively mild conditions.[1—12] Depending on the structure of the initial azinium salt, the nature of the attacking nucleophile, and reaction conditions, azinium salts can transform into σ^H-adducts and products of nucleophilic substitution of hydrogen S_N^H or undergo deeper transformations (Scheme 1).

Scheme 1



X, Y = CH, N
EWG is electron-withdrawing group, Nu is nucleophile

We have earlier carried out the series of works on studying the properties of substituted pyrazinium salts.[6—12] It was shown that they are capable of reacting with various types of nucleophiles under mild conditions to form products of nucleophile addition to unsubstituted positions of the heterocycle.

In the present work, we studied the possibility of using substituted phenols as nucleophiles. It is known that the phenol derivatives are efficient antioxidants. Among the modern inhibitors of free-radical oxidation of organic and bioorganic substrates, antioxidants of the phenol type play the leading role: stabilizers of plastics, rubbers, and caoutchoucs; the most part of food antioxidants and drugs with antioxidant effect are also phenol compounds.[13—24] It seemed interesting to study the possibility of direct cross-coupling of 1,4-diazinium systems with phenol derivatives aimed at developing new types of compounds with antioxidant activity.

There are published data on the reactions of 1,2,4-triazinium and 1,3-diazinium salts with resorcinol.[25—28] Information on the reactions of pyrazinium salts with phenol derivatives are almost absent, and only the single example of the reaction of 2,3-dichloro-1-ethylpyrazinium with resorcinol was described.[29] In particular, it was shown that protic salts of 3-substituted 1,2,4-triazines **1** are transformed into benzofurotriazines **2**, whereas the reaction of azolopyrimidinium salts **3** with resorcinol is completed by the formation of framework structures, derivatives of oxazocines **4** (Scheme 2).

In this work, quaternary salts of 5-(het)aryl-2,3-dicyano-1-ethylpyrazinium **5a,b** and protic salts of 1,2,5-oxadiazolo[3,4-*b*]pyrazinium were chosen as substrates.

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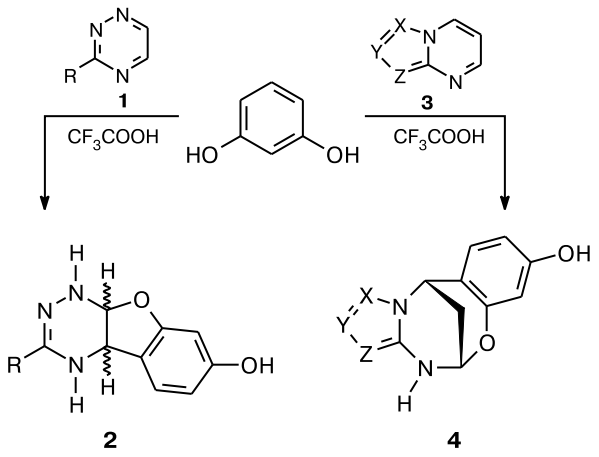
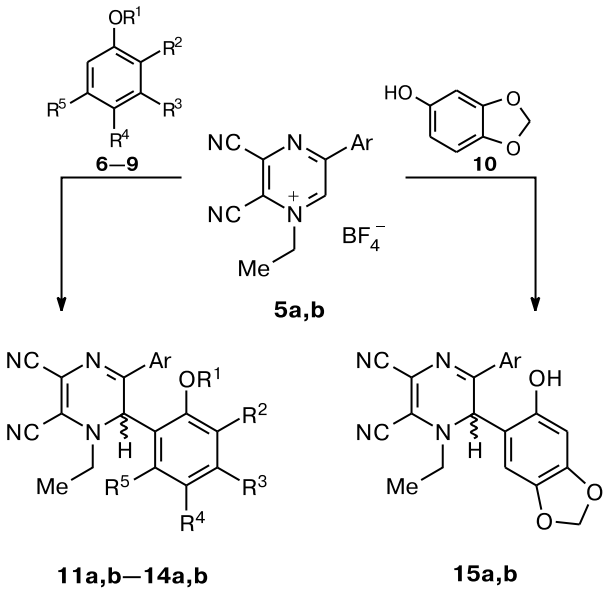
Scheme 2



X, Y, Z = CH, N

Salts of 5-(het)aryl-2,3-dicyano-1-ethylpyrazinium **5a,b** were shown to react easily with resorcinol (**6**), pyrogallol (**7**), phloroglucinol (**8**) and its trimethyl ester (**9**), and natural antioxidant sesamol (**10**) under mild conditions (CH_3CN, 20—25 °C), giving σ^H-adducts **11a**,**b**—**15a**,**b** to the position C(6) (Scheme 3). The structures of synthesized 1,2-dihydropyrazines **11**—**15** were unambiguously confirmed by X-ray diffraction data (Fig. 1, Tables 1 and 2).

Scheme 3



Ar = Ph (**a**), thiophen-3-yl (**b**)

6, 11: $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OH$
7, 12: $R^1 = R^4 = R^5 = H$, $R^2 = R^3 = OH$
8, 13: $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = OH$
9, 14: $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = R^5 = OMe$

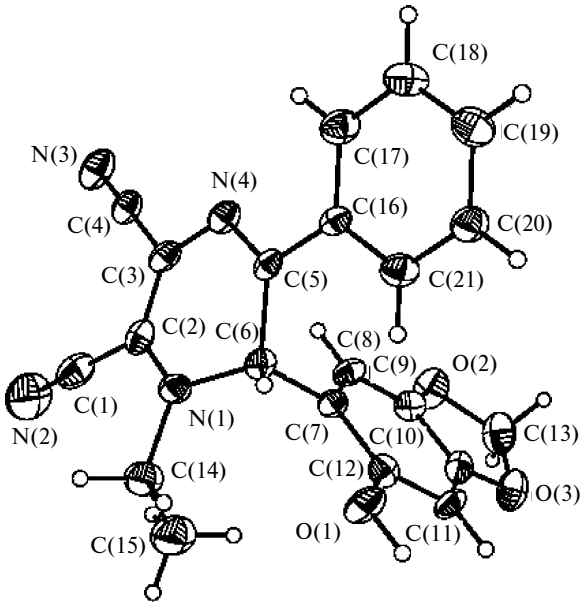


Fig. 1. X-ray structure of compound **15a**.

According to the X-ray diffraction data, adducts **11a**, **12a**, **14a**, and **15a** crystallize in centrosymmetric space groups of various crystallographic systems (see Table 1). The general geometry of the dihydroazine fragments of the obtained adducts is close to the geometry of the adducts studied earlier[8—12] and is determined by the presence of the system of conjugated multiple bonds of the cyano groups and dihydroazine cycle. Compounds **11a** and **12a** are characterized by the *trans*-orientation of the polyhydroxyarene fragment and group N—Et relative to the root-mean-square plane of dihydroazine; compounds **14a** and **15a** are characterized by *cis*-orientation. Stereometry of the molecular packing is determined by the presence of the system of intramolecular hydrogen bonds and intermolecular hydrogen bonds (see Table 1) and a series of shortened contacts. So, the crystals of compounds **11a** and **15a** contain intermolecular hydrogen bonds O—H...N≡C— joining the molecules into polymer chains of similar geometry. The orientation of the chain of molecules of compound **11a** coincides with the translation chain 0*b*, and the chains of compounds **15a** lie on the sliding refection planes. The most developed system of hydrogen bonds is observed in the packing of compound **12a**. It includes intramolecular hydrogen bonds O—H...O in the polyhydroxyaryl substituent and intermolecular hydrogen bonds between the OH and CN groups and the nitrogen atom of the dihydroazine cycle. As a result, a packing as double chains of molecules parallel to the axis *a*—*b* is formed. The molecules of the chains are brought together, and the shortened π—π-contact (the distance between the atoms C(15)...C(15) [$-x$, $-y$, $1-z$] is 3.370 Å) is observed between the polyhydroxyaryl fragments.

Table 1. Parameters of hydrogen bonds D—H...A in molecular packings according to the X-ray diffraction data

Compound	D—H	*d*(D—H)	*d*(H...A)	*d*(D...A)	D—H—A /deg	A
		Å				
11a	O(2)—H(2)	0.82(3)	1.92(3)	2.736(3)	177(1)	O(2S)
	O(1)—H(1)	0.86(3)	2.03(3)	2.884(3)	174(1)	N(3) [x, $y-1$, z]
12a	O(3)—H(3)	0.96(3)	2.14(3)	3.025(3)	153(1)	N(4) [$x-1/2$, $y+1/2$, z]
	O(3)—H(3)	0.96(3)	2.23(3)	2.719(3)	110(1)	O(2)
	O(1)—H(1)	0.87(3)	2.03(3)	2.895(3)	170(1)	N(3) [$-x+1/2$, $-y-1/2$, $-z+1$]
	O(2)—H(2)	0.92(3)	2.21(3)	2.700(3)	113(1)	O(1)
	O(2)—H(2)	0.92(3)	2.29(3)	3.093(3)	146(1)	N(2) [x, $y+1$, z]
15a	O(1)—H(1)	0.91(3)	1.96(3)	2.862(3)	174(1)	N(3) [$x+1$, $-y+1/2$, $z-1/2$]
36a	O(2)—H(2)	0.75(3)	2.45(3)	2.969(2)	128(1)	N(2) [x, $-y+3/2$, $z+1/2$]
45a	N(2)—H(2)	0.80(2)	2.17(2)	2.961(3)	169(2)	O(1S)
	N(4)—H(4B)	0.84(3)	2.24(3)	3.065(3)	169(2)	N(3) [$-x+3/2$, $y-1/2$, $-z-1/2$]
	N(4)—H(4A)	0.89(2)	2.14(3)	3.006(4)	163(2)	O(1S)
	O(1S)—H(1S)	0.91(3)	2.03(3)	2.880(3)	154(3)	N(1) [x, $y-1$, z]
	O(1S)—H(1S)	0.91(3)	2.58(3)	3.291(3)	135(2)	O(2) [x, $y-1$, z]
46a	N(2)—H(2A)	0.860	2.297	3.065(7)	148.82	N(4) [$-x+1/2$, $y+1/2$, $-z-1/2$]

Attempts to carry out similar reactions with unsubstituted 2,3-dicyano-1-ethylpyrazinium salt and with 5-(het)aryl-1,2,5-oxadiazolo[3,4-*b*]pyrazines **16a**,**b** in the presence of CF_3COOH were unsuccessful, because they resulted in complicated multicomponent mixtures (according to the TLC data).

The products of the reactions of 5-(het)aryl-1,2,5-oxadiazolo[3,4-*b*]pyrazines **16a**,**b** (Scheme 4) with sterically hindered phenols **18**—**20**, their methyl esters **9** and **21**, **23**, **24**, and 2-naphthol (**25**) and its methyl ester **22** depend on the structure of reacting phenol.

In the reactions with 2,6-dimethyl- (**18**), 2,6-di-*tert*-butyl- (**19**), and 2-isobornyl-6-methylphenols (**20**), as well as with dimethyl ester of resorcinol (**21**), trimethyl ester of phloroglucine (**9**), and methyl ester of 2 naphthol (**22**), 1,2-dihydropyrazines **26**—**31** are spontaneously oxidized with air oxygen to the corresponding aromatic S_NH products **35**—**36a**,**b**, **37a**, and **38**—**40a**.

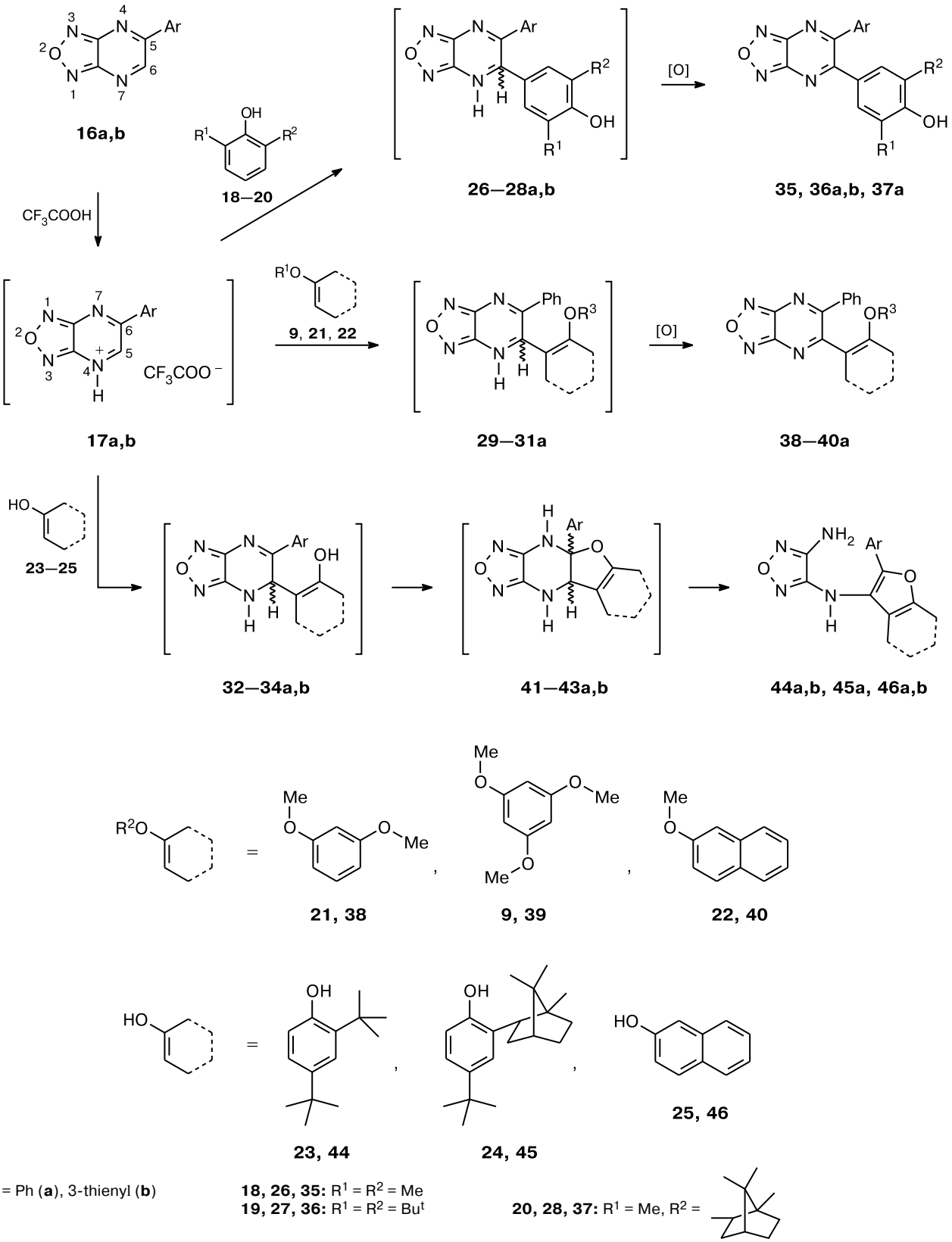
At the same time, the reactions of 2,4-di-*tert*-butylphenol (**23**), 2-isobornyl-4-methylphenol (**24**), and naphthol (**25**) gave unexpected benzo[*b*]furan derivatives as products: *N*-(2-(het)aryl-5,7-di-*tert*-butylbenzofuran-3-yl)furazan-3,4-diamines **44a,b**, *N*-(5-isobornyl-7-methyl-2-phenylbenzofuran-3-yl)furazan-3,4-diamine **45a**, and *N*-(2-(het)arylnaphtho[2,1-*b*]furan-1-yl)furazan-3,4-diamines **46a**,**b**. Their formation can be explained by the further transformations of 1,2-dihydropyrazines **32**—**34a**,**b** formed at the first stage into the corresponding 1,2,3,4-tetrahydropyrazines **41**—**43a**,**b**, which are transformed, in turn, into benzofuran derivatives **44**—**46** due to tetrahydropyrazine ring opening (see Scheme 4). It is most probable that the reactions of furazanopyrazinium protic salts with polyphenols proceed through the intermediate formation of C-adducts **26**—**34** to the position C(5); however, σ^H-adducts **26**—**34** are unstable and undergo further transformations.

The differences in the behavior of the σ^H-adducts can be explained by their structure. Phenols with the unsubstituted *ortho*-position to the OH group act as 1,3-C,O-dinucleophiles and produce the corresponding monoadducts **32**—**34**, which undergo further transformations into more stable benzofurans **41**—**43**. In the case of phenols having no free *ortho*-position to the OH group or their methyl esters. monoadducts are formed and their further stabilization occurs due to the formation of aromatic furazanopyrazines **35**—**40**.

As shown previously,[8] *N*-ethyl salts of 2,3-dicyanopyrazinium are characterized by comparatively stable monoadducts and, hence, the reactions cease at the stage of formation of 1,2-dihydropyrazines **11**—**15**.

The structures of S_NH product **36a** and open-chain compounds **45a** and **46a** were confirmed by the X-ray diffraction data. The general views of the molecules are presented in Figs 2 and 3. The main parameters of structural experiments are listed in Table 2. Compound **36a** crystallizes in the centrosymmetric space group of orthorhombic crystal system. The phenyl and hydroxyphenyl substituents of the azine cycle exhibit non-coplanar unfolding relative to the pyrazine cycle plane due to the steric influence of the *tert*-butyl groups. The molecular packing is characterized by the intermolecular hydrogen bonds between the OH group of the hydroxyphenyl substituent and the nitrogen atom of the azine cycle, due to which the molecules are packed into polymer ribbons extended along the axis 0*c*. In this case, shortened π—π-contacts (the distance C(4)...C(4) [$-x$, $1-y$, $-z$] is 3.292(3) Å, which is 0.108 Å shorter than the sum of van der Waals radii) appear between the 1,2,5-oxadiazo-

Scheme 4



Ar = Ph (**a**), 3-thienyl (**b**)

18, 26, 35: $R^1 = R^2 = Me$
19, 27, 36: $R^1 = R^2 = Bu^t$

20, 28, 37: $R^1 = Me$, $R^2 =$

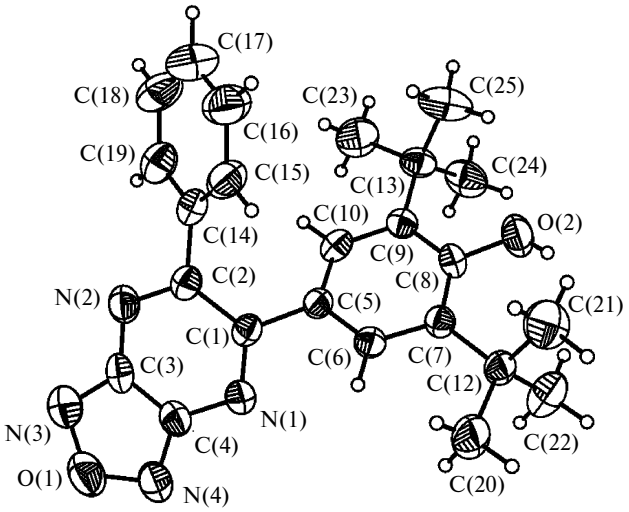


Fig. 2. General view of compound **36a** in thermal ellipsoids of 50% probability according to the X-ray diffraction data.

lo[3,4-*b*]pyrazine fragments of molecules of the adjacent chains.

Compound **45a** crystallizes in the centrosymmetric space group of monoclinic crystal system as a solvate with an EtOH molecule (Table 2). The phenyl substituent of the benzofuran fragment is unfolded relative to its plane at an angle of 13.0°, and the oxadiazole fragment is unfolded at an angle of 73.2°. The molecular packing is characterized by the system of intermolecular hydrogen bonds involving the OH group of EtOH, the NH_2 group, and the nitrogen atoms of the oxadiazole cycle (see Table 2), due to which the molecules are packed into polymer ribbons extended along the axis 0*b*.

The low quality of the crystal of compound **46a** presented for X-ray diffraction analysis allows only rough estimation of its structure to perform. Compound **46a** crystallizes in the centrosymmetric space group of monoclinic crystal system. The phenyl substituent of the benzofuran cycle is unfolded relative to its plane at an angle of 14.5°,

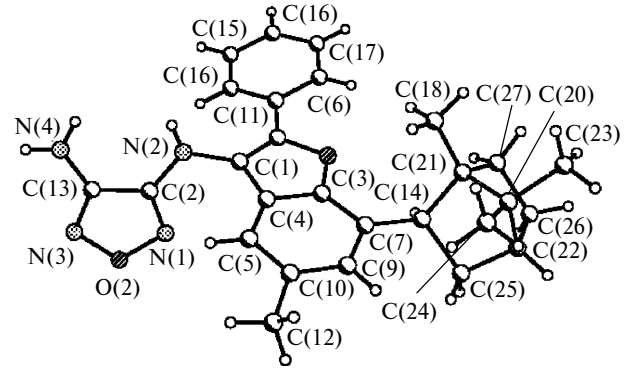


Fig. 3. General view of compound **45a** according to the X-ray diffraction data.

and the oxadiazole fragment is unfolded at an angle of 69.5°. The molecules are packed into polymer spiral ribbons arranged on the screw 2-fold axis by intermolecular hydrogen bonds of the N—H...N type (see Table 1). A rather unusual N—H...π contact is observed between molecules of the ribbons between the secondary amino group of the molecule and one of the rings of the naphthalene system (the distance from the centroid C(4)C(5)C(6)C(7)C(8)C(9) [x, $-1 + y$, z] to the atom N(1) is 3.309(7) Å and that to the atom H(1) is 2.40(6) Å; contact angle 152(3)°, which is comparable with the hydrogen bond parameters).

Thus, tandem reactions giving the products of 1,4-diazine ring opening are discovered in the reactions of pyrazinium salts with polyphenols along with the formation of comparatively stable C-adducts at the activated C=N bond or the products of aromatic hydrogen nucleophilic substitution. The reaction proceeds *via* one of the possible routes depending on the nature and arrangement of substituents in the phenol derivatives.

Experimental

Solvents and reagents were dried and purified according to the literature procedures.[30] The initial compounds **5a,b** and **16a** were synthesized according to procedures described earlier.[8,31]

^{1}H NMR spectra were recorded on a Bruker DRX-400 instrument with a working frequency of 400 MHz using $SiMe_4$ as an internal standard. Elemental analysis was carried out on a Perkin—Elmer PE-2400 automated analyzer. Melting points were determined on Boetius combined heating stages and no corrections were applied. Flash chromatography was carried out using silica gel Lancaster 0.040—0.063 mm (230—400 mesh).

The reaction course and purity of the products were monitored by TLC on the plates Sorbfil developing under UV irradiation or I_2 vapors.

The X-ray diffraction studies were carried out on an Xcalibur-3 X-ray diffractometer with a CCD detector using a standard procedure (λMo-Kα, graphite monochromator, ω scan mode). The structures of all compounds were solved by a direct method using the SHELXS-97 program and refined using the SHELXL-97 program in the anisotropic (isotropic for hydrogen atoms) approximation.[32] No absorption correction was applied. Selected parameters of structural experiments are listed in Table 2. The results of X-ray diffraction studies* were deposited with the Cambridge Crystallographic Data Centre as *cif* files (CCDC Nos 816 956 (compound **11a**), 816 957 (compound **12a**), 816 959 (compound **14a**), 816 958 (compound **15a**), 816 961 (compound **36a**), 816 962 (compound **45a**), and 816 960 (compound **46a**).**

5-(3-Thienyl)-1,2,5-Oxadiazolo[3,4-*b*]pyrazine (16b). 3,4-Diaminofurazan (1 g, 10 mmol) and 3-thienylglyoxal (1.4 g,

* The X-ray diffraction results were obtained for seven compounds. However, only three significant figures are presented in the article because of their resemblance and low information content.

** These materials are available free of charge and can be requested at www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Selected parameters of X-ray diffraction experiments

Compound	**11a**	**12a**	**14a**	**15a**	**40a**	**45a**	**46a**
Formula	$C_{24}H_{24}N_4O_4$	$C_{20}H_{16}N_4O_3$	$C_{23}H_{22}N_4O_3$	$C_{21}H_{16}N_4O_3$	$C_{24}H_{26}N_4O_2$	$C_{29}H_{36}N_4O_3$	$C_{20}H_{14}N_4O_2$
Crystal size/mm	0.49×0.25×0.08	0.39×0.28×0.16	0.26×0.20×0.17	0.27×0.13×0.04	0.49×0.31×0.08	0.25×0.20×0.15	0.51×0.14×0.02
Color	Yellow	Yellow	Orange	Yellow	Red	Colorless	Colorless
Temperature of experiment/K	295(2)	295(2)	295(2)	145(2)	295(2)	295(2)	295(2)
Molecular weight	432.47	360.37	402.45	372.38	402.49	488.62	342.35
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/n$	$P2_1$/c	*Pbca*	$P2_1/n$	*C*2/*c*
a/Å	8.2818(13)	12.4003(11)	9.0773(8)	6.6317(7)	19.3830(15)	13.7472(16)	37.520(8)
b/Å	10.8753(19)	10.7416(11)	17.3191(12)	17.5180(17)	10.9693(10)	7.2538(6)	5.6074(11)
c/Å	13.407(2)	27.163(3)	14.1333(8)	15.5220(15)	20.4982(19)	27.544(3)	15.293(4)
α/deg	75.323(16)	90	90	90	90	90	90
β/deg	81.915(14)	100.521(8)	105.871(6)	96.913(8)	90	102.977(10)	95.021(19)
γ/deg	82.572(14)	90	90	90	90	90	90
V/Å^3	1151.0(3)	3557.3(6)	2137.2(3)	1790.1(3)	4358.3(7)	2676.5(5)	3205.2(13)
Z	2	8	4	4	8	4	8
d_{calc}	1.248	1.346	1.251	1.382	1.227	1.213	1.419
μ/mm^{-1}	0.087	0.094	0.085	0.095	0.080	0.079	0.095
Scan range/deg	2.80 < θ < 28.28	3.11 < θ < 26.38	2.79 < θ < 28.29	2.64 < θ < 26.38	2.80 < θ < 26.37	2.91 < θ < 26.37	2.80 < θ < 26.37
Number of measured reflections	10215	8005	13256	8762	14937	12694	5826
Number of independent reflections (R_{int})	5286 (0.0227)	3508 (0.0412)	5191 (0.0224)	3529 (0.0567)	4453 (0.0682)	5462 (0.0393)	3126 (0.0699)
Number of reflections with $I > 2\sigma(I)$	2276	1962	2551	1662	1687	1882	1292
Completeness (for θ/deg)	96.5 (26.00)	96.6 (26.00)	98.0 (28.29)	96.2 (26.38)	99.9 (26.37)	99.9 (26.37)	96.3 (25.50)
S	1.000	1.004	1.016	0.917	0.960	1.010	0.992
Number of refined parameters	310	278	275	257	281	359	239
R_1 (on $I > 2\sigma(I)$)	0.0399	0.0455	0.0398	0.0409	0.0354	0.0450	0.0791
wR_2 (on $I > 2\sigma(I)$)	0.0795	0.0972	0.0966	0.0354	0.0316	0.0890	0.1800
R_1 (on all reflections)	0.1129	0.0879	0.0903	0.1246	0.1242	0.1271	0.1887
wR_2 (on all reflections)	0.0866	0.1044	0.1044	0.0397	0.0337	0.0938	0.2025
(ρ_{max}/ρ_{min})/e Å^{-3}	0.145/−0.198	0.168/−0.157	0.168/−0.180	0.208/−0.196	0.146/−0.181	0.345/−0.175	0.323/−0.193

10 mmol) were refluxed for 1 h in a mixture of EtOH (4 mL) and glacial acetic CH_3COOH (4 mL). At the end of the reaction, the mixture was cooled down, and the precipitate that formed was filtered off and washed with ethanol. The product was obtained as a dark yellow crystalline powder. The yield was 68%, m.p. 166—168 °C. ^{1}H NMR (DMSO-d_6), δ: 7.86 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 8.01 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.2 Hz); 9.05, 7.81 (both dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz); 9.76 (s, 1 H, C6(H)). Found (%): C, 47.15; H, 2.03; N, 27.64. $C_8H_4N_4OS$. Calculated (%): C, 47.05; H, 1.97; N, 27.44.

Synthesis of 6-substituted 5-(het)aryl-1-ethyl-1,6-dihydropyrazine-2,3-dicarbonitriles 11a,b—15a,b (general procedure). A solution of salt **5a** or **5b** (1.2 mmol) and phenol derivative **6** or **7—10** (1 mmol) in anhydrous MeCN (5—7 mL) was stirred for 1 h at room temperature, the solvent was distilled *in vacuo*, and the residue was chromatographed eluting with an ethyl acetate—hexane (1 : 1) mixture. If necessary, the obtained product was additionally recrystallized from an EtOH—H_2O (1 : 1) mixture.

6-(2,4-Dihydroxyphenyl)-1-ethyl-5-phenyl-1,6-dihydropyrazine-2,3-dicarbonitrile (11a). Product **11a** was obtained as an orange crystalline powder. The yield was 95%, m.p. 198—201 °C (decomp.).^{1}H NMR (CD_3CN), δ: 1.20 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.58 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.71 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 6.19 (s, 1 H, C(6)$\underline{H}$); 6.27 (dd, 1 H, C_{arom}(H(5′)), J = 8.5 Hz, J = 2.4 Hz); 6.40 (d, 1 H, C_{arom}(H(3′)), J = 2.4 Hz); 6.84 (d, 1 H, C_{arom}(H(6′)), J = 8.5 Hz); 7.11 (s, 1 H, OH); 7.39—7.46 (m, 3 H, Ph); 7.71 (s, 1 H, OH); 7.86—7.88 (m, 2 H, Ph). Found (%): C, 67.57; H, 4.99; N, 15.61. $C_{20}H_{16}N_4O_2 \cdot 0.67\ H_2O$. Calculated (%): C, 67.42; H, 4.89; N, 15.73.

6-(2,4-Dihydroxyphenyl)-1-ethyl-5-(3-thienyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (11b) was obtained as a yellow crystalline powder. The yield was 95%, m.p. 180—182 °C (decomp.). ^{1}H NMR (CD_3CN), δ: 1.19 (t, 3 H, C$\underline{H}_3$, J = 7.2); 3.53 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.59 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 6.07 (s, 1 H, C(6)$\underline{H}$); 6.30 (dd, 1 H, C_{arom}(H(5′)), J = 8.5 Hz, J = 2.4 Hz); 6.38 (d, 1 H, C_{arom}(H(3′)), J = 2.4 Hz); 6.91 (d, 1 H, C_{arom}(H(6′)), J = 8.5 Hz); 7.12 (s, 1 H, OH); 7.27 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 7.58 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.3 Hz); 7.71 (s, 1 H, OH); 7.87 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.3 Hz). Found (%): C, 61.36; H, 4.06; N, 15.79. $C_{18}H_{14}N_4O_2S$. Calculated (%): C, 61.70; H, 4.03; N, 15.99.

6-(2,3,4-Dihydroxyphenyl)-1-ethyl-5-phenyl-1,6-dihydropyrazine-2,3-dicarbonitrile (12a) was obtained as a yellow crystalline powder. The yield was 60%, m.p. 205—207 °C (decomp.). ^{1}H NMR (CD_3CN), δ: 1.21 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.59 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.72 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 6.20 (s, 1 H, C(6)$\underline{H}$); 6.35 (d, 1 H, C_{arom}(H(6′)), J = 8.5 Hz); 6.45 (d, 1 H, C_{arom}(H(5′)), J = 8.5 Hz); 6.91 (br.s, 3 H, OH); 7.38—7.45 (m, 3 H, Ph); 7.86—7.88 (m, 2 H, Ph). Found (%): C, 66.65; H, 4.46; N, 15.61. $C_{20}H_{16}N_4O_3$. Calculated (%): C, 66.66; H, 4.48; N, 15.55.

6-(2,3,4-Dihydroxyphenyl)-1-ethyl-5-(3-thienyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (12b) was obtained as a yellow crystalline powder. The yield was 62%, m.p. 224—226 °C (decomp.). ^{1}H NMR (CD_3CN), δ: 1.19 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.55 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.62 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 6.08 (s, 1 H, C(6)$\underline{H}$); 6.37 (d, 1 H, C_{arom}(H(6′)), J = 8.5 Hz); 6.52 (d, 1 H, C_{arom}(H(5′)), J = 8.5 Hz); 7.02 (br.s, 3 H, OH); 7.41 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 7.58 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.3 Hz); 7.87 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.3 Hz). Found (%): C, 58.76; H, 3.70; N, 15.04. $C_{18}H_{14}N_4O_3S$. Calculated (%): C, 59.01; H, 3.85; N, 15.29.

1-Ethyl-5-phenyl-6-(2,4,6-trihydroxyphenyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (13a) was obtained as a dark yellow crystalline powder. The yield was 67%, m.p. 200—201 °C (decomp.). ^{1}H NMR (CD_3CN), δ: 1.16 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.33 (dq, 2 H, NCH_2, J = 14.4 Hz, J = 7.2 Hz); 5.89 (s, 2 H, C_{arom}(H(3′)), C_{arom}(H(5′))); 6.46 (s, 1 H, C(6)$\underline{H}$); 7.00 (s, 1 H, C_{arom}(4′)OH); 7.32—7.39 (m, 3 H, Ph); 7.50 (s, 2 H, C_{arom}(2′)OH, C_{arom}(6′)OH); 7.89—7.91 (m, 2 H, Ph). Found (%): C, 66.56; H, 4.37; N, 15.44. $C_{20}H_{16}N_4O_3$. Calculated (%): C, 66.66; H, 4.48; N, 15.55.

1-Ethyl-5-(3-thienyl)-6-(2,4,6-trihydroxyphenyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (13b) was obtained as an orange crystalline powder. The yield was 95%, m.p. 198—201 °C (decomp.). ^{1}H NMR (CD_3CN), δ: 1.14 (t, 3 H, C$\underline{H}_3$, J = 7.3 Hz); 3.31 (dq, 2 H, NCH_2, J = 14.6 Hz, J = 7.3 Hz); 5.92 (s, 2 H, C_{arom}(H(3′)), C_{arom}(H(5′))); 6.34 (s, 1 H, C(6)$\underline{H}$); 7.03 (s, 1 H, C_{arom}(4′)OH); 7.34 (dd, 1 H, H(5″)-3-thienyl, J = 5.1 Hz, J = 2.8 Hz); 7.55—7.56 (m, 3 H, H(4″)-3-thienyl, C_{arom}(2′)OH, C_{arom}(6′)OH); 7.93 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz). Found (%): C, 57.50; H, 3.96; N, 14.61. $C_{18}H_{14}N_4O_3S \cdot 0.5H_2O$. Calculated (%): C, 57.59; H, 4.03; N, 14.92.

1-Ethyl-5-phenyl-6-(2,4,6-trimethoxyphenyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (14a). was obtained as an orange crystalline powder. The yield was 79%, m.p. 192—195 °C. ^{1}H NMR (CD_3CN), δ: 1.14 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.27 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.36 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 3.76 (s, 3 H, C_{arom}(4′)OCH_3); 3.87 (s, 6 H, C_{arom}(2′)OCH_3, C_{arom}(6′)OCH_3); 6.20 (s, 2 H, C_{arom}(H(3′)), C_{arom}(H(5′))); 6.58 (s, 1 H, C(6)$\underline{H}$); 7.32—7.38 (m, 3 H, Ph); 7.82—7.85 (m, 2 H, Ph). Found (%): C, 68.68; H, 5.57; N, 13.82. $C_{23}H_{22}N_4O_3$. Calculated (%): C, 68.64; H, 5.51; N, 13.92.

1-Ethyl-5-(3-thienyl)-6-(2,4,6-trimethoxyphenyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (14b) was obtained as a dark yellow crystalline powder. The yield was 70%, m.p. 206—207 °C. ^{1}H NMR (CD_3CN), δ: 1.12 (t, 3 H, C$\underline{H}_3$, J = 7.2 Hz); 3.23 (dq, 1 H, NCH^A, J = 14.4 Hz, J = 7.2 Hz); 3.32 (dq, 1 H, NCH^B, J = 14.4 Hz, J = 7.2 Hz); 3.78 (s, 3 H, C_{arom}(4′)OCH_3); 3.88 (s, 6 H, C_{arom}(2′)OCH_3, C_{arom}(6′)OCH_3); 6.23 (s, 2 H, C_{arom}(H(3′)), C_{arom}(H(5′))); 6.46 (s, 1 H, C(6)$\underline{H}$); 7.34 (dd, 1 H, H(5″)-3-thienyl, J = 5.2, J = 2.8 Hz); 7.52 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.3 Hz); 7.81 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz). Found (%): C, 61.54; H, 4.77; N, 13.81. $C_{21}H_{20}N_4O_3S$. Calculated (%): C, 61.75; H, 4.94; N, 13.72.

1-Ethyl-6-(6-hydroxybenzo[1,3]dioxol-5-yl)-5-phenyl-1,6-dihydropyrazine-2,3-dicarbonitrile (15a) was obtained as a dark yellow crystalline powder. The yield was 51%, m.p. 216—217 °C. ^{1}H NMR ($CDCl_3$), δ: 1.26 (t, 3 H, C$\underline{H}_3$, J = 7.1 Hz); 3.70 (dq, 2 H, NCH_2, J = 14.2 Hz, J = 7.1 Hz); 5.38 (br.s, 1 H, C_{arom}(6′)OH); 5.88 (br.s, 1 H, C_{arom}(2′)H^A); 5.91 (br.s, 1 H, C_{arom}(2′)H^B); 6.16 (s, 1 H, C(6)$\underline{H}$); 6.42, 6.45 (two s, 2 H, C_{arom}(H(4′)), C_{arom}(H(7′))); 7.36—7.44 (m, 3 H, Ph); 7.88—7.90 (m, 2 H, Ph). Found (%): C, 67.64; H, 4.09; N, 15.08. $C_{21}H_{16}N_4O_3$. Calculated (%): C, 67.73; H, 4.33; N, 15.05.

1-Ethyl-6-(6-hydroxybenzo[1,3]dioxol-5-yl)-5-(3-thienyl)-1,6-dihydropyrazine-2,3-dicarbonitrile (15b) was obtained as

a yellow crystalline powder. The yield was 72%, m.p. 185—187 °C. ^{1}H NMR ($CDCl_3$), δ: 1.27 (t, 3 H, C<u>H</u>$_3$, J = 7.2 Hz); 3.63 (dq, 2 H, NC<u>H</u>$_2$, J = 14.2 Hz, J = 7.1 Hz); 5.74 (br.s, 1 H, C_{arom}(6′)O<u>H</u>); 5.89 (br.s, 1 H, C_{arom}(2′)H^A); 5.91 (br.s, 1 H, C_{arom}(2′)H^B); 6.08 (s, 1 H, C(6)<u>H</u>); 6.43, 6.51 (both s, 2 H, C_{arom}(H(4′)), C_{arom}(H(7′))); 7.30 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 7.66 (br.d, 1 H, H(4″)-3-thienyl, J = 5.2 Hz); 7.80 (br.d, 1 H, H(2″)-3-thienyl, J =1.2). Found (%): C, 60.14; H, 3.97; N, 15.00. $C_{19}H_{14}N_4O_3S$. Calculated (%): C, 60.31; H, 3.73; N, 14.81.

Synthesis of 2,6-disubstituted 4-(6-(het)aryl-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl)phenols 35a,b, 36a,b, and 37a (general procedure). 2,6-Disubstituted phenol (1 mmol) dissolved in trifluoroacetic acid (2 mL) was added with stirring to a solution of 6-(het)arylfurazano[3,4-*b*]pyrazine (1 mmol) in trifluoroacetic acid (2 mL). The reaction mixture was stored from 15 min to 2 h (TLC monitoring) and diluted with water. The precipitate that formed was filtered off, washed with water several times, and recrystallized from ethanol. In the case of products **35a** and **36b**, the mixture was separated by chromatography eluting with an ethyl acetate—hexane (1 : 2) mixture.

2,6-Dimethyl-4-(6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl)phenol (35a). Product **35a** was obtained as a yellow-orange crystalline powder. The yield was 55%, m.p. 207—208 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 2.05 (s, 6 H, CH_3); 7.05 (s, 2 H, Ar); 7.40—7.52 (m, 5 H, Ar); 9.02 (s, 1 H, OH). Found (%): C, 67.77; H, 4.55; N, 17.52. $C_{18}H_{14}N_4O_2$. Calculated (%): C, 67.91; H, 4.43; N, 17.6.

2,6-Dimethyl-4-[6-(3-thienyl)-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl]phenol (35b) was obtained as a yellow-orange crystalline powder. The yield was 41%, m.p. 201—203 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 2.13 (s, 6 H, CH_3); 7.14—7.16 (m, 3 H, H(4″)-3-thienyl, C_{arom}(H(3′)), C_{arom}(H(5′))C); 7.58 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 7.77 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz); 9.02 (s, 1 H, OH). Found (%): C, 59.54; H, 3.55; N, 17.52. $C_{16}H_{12}N_4O_2S$. Calculated (%): C, 59.25; H, 3.73; N, 17.27.

2,6-Di-*tert*-butyl-4-(6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl)phenol (36a) was obtained as an orange crystalline powder. The yield was 75%, m.p. 220—222 °C. ^{1}H NMR (DMSO-d_6), δ: 1.23 (s, 18 H, Bu^t); 7.32 (s, 2 H, Ar); 7.43—7.51 (m, 5 H, Ar); 7.62 (s, 1 H, OH). Found (%): C, 71.25; H, 6.43; N, 13.8. $C_{24}H_{26}N_4O_2$. Calculated (%): C, 71.62; H, 6.51; N, 13.92.

2,6-Di-*tert*-butyl-4-[6-(3-thienyl)-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl]phenol (36b) was obtained as a yellow-orange crystalline powder. The yield was 68%, m.p. 192—194 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 1.31 (s, 18 H, Bu^t); 7.00 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.2 Hz); 7.38 (s, 2 H, Ar); 7.59 (dd, 1 H, H(5″)-3-thienyl, J = 5.0 Hz, J = 2.8 Hz); 7.7 (s, 1 H, OH); 7.80 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz). Found (%): C, 64.50; H, 5.99; N, 13.8. $C_{22}H_{24}N_4O_2S$. Calculated (%): C, 64.68; H, 5.92; N, 13,71.

2-Methyl-4-(6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazin-5-yl)-6-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)phenol (37a) was obtained as an orange crystalline powder. The yield was 47%, m.p. 231 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 0.42 (s, 3 H, CH_3); 0.60 (s, 3 H, CH_3); 0.71 (s, 3 H, CH_3); 1.21—1.27 (m, 2 H, Alk); 1.4—1.54 (m, 3 H, Alk); 1.64—1.76 (m, 2 H, Alk); 2.2 (s, 3 H, CH_3); 3.15 (t, 1 H, J = 8.4 Hz); 7.03 (d, 1 H, Ar, J = 2.0 Hz); 7.32 (d, 1 H, Ar, J = 2.0 Hz); 7.37—7.48 (m, 5 H, Ph); 8.85 (br.s, 1 H, OH). Found (%): C, 73.74; H, 6.59; N, 12.55. $C_{27}H_{28}N_4O_2$. Calculated (%): C, 73.61; H, 6.41; N, 12.72.

Synthesis of 5-aryl-6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazines 38a, 39a, and 40a (general procedure). A solution of methoxylated resorcinol, phloroglucine, or 2-naphthol (1 mol) in benzene (2—3 mL) was added to a solution of 6-phenylfurazano-[3,4-*b*]pyrazine (1 mmol) in anhydrous benzene (3 mL). Several droplets of boron trifluoride etherate were added to the obtained mixture, and the resulting solution was left to stay for 2—3 h. The reaction mixture was concentrated by evaporation, washed with a solution of sodium hydrocarbonate, and recrystallized from isopropyl alcohol.

5-(2,4-Dimethoxyphenyl)-6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazine (38a). Product **38a** was obtained as a yellow crystalline powder. The yield was 62%, m.p. 128—130 °C. ^{1}H NMR (DMSO-d_6), δ: 3,09 (s, 3 H, OCH_3); 3.81 (s, 3 H, OCH_3); 6.38 (br.s, 1 H, C_{arom}(H(3′)); 6.78 (br.d, 1 H, C_{arom}(H(5′)), J = 8.0 Hz); 7.33—7.45 (m, 5 H, Ph); 7.64 (br.d, 1 H, C_{arom}(H(6′)), J = 8.0 Hz). Found (%): C, 64.5; H, 4.16; N, 17.01. $C_{18}H_{14}N_4O_3$. Calculated (%): C, 64.66; H, 4.22; N, 16.76.

6-Phenyl-5-(2,4,6-trimethoxyphenyl)-1,2,5-oxadiazolo[3,4-*b*]pyrazine (39a) was obtained as a yellow crystalline powder. The yield was 60%, m.p. 133—136 °C. ^{1}H NMR (DMSO-d_6), δ: 3.33 (s, 6 H, C_{arom}(2′)OCH_3, C_{arom}(6′)OCH_3); 3.79 (s, 3 H, C_{arom}(4′)OCH_3); 6.23 (s, 2 H, C_{arom}(H(3′)), C_{arom}(H(5′))); 7.34—7.48 (m, 5 H, Ph). Found (%): C, 62.81; H, 4.36; N, 15.41. $C_{19}H_{16}N_4O_4$. Calculated (%): C, 62.63; H, 4.43; N, 15.38.

5-(2-Methoxynaphthalen-1-yl)-6-phenyl-1,2,5-oxadiazolo[3,4-*b*]pyrazine (40a) was obtained as an orange-red crystalline powder. The yield was 52%, m.p. 228—230 °C. ^{1}H NMR (DMSO-d_6), δ: 3.37 (s, 3 H, OCH_3); 7.19—7.26 (m, 2 H, Ph); 7.28—7.32 (m, 3 H, Ph); 7.35—7.38 (m, 1 H, naphthyl); 7.46—7.49 (m, 1 H, naphthyl); 7.54—7.58 (m, 1 H, naphthyl); 7.97—7.99 (m, 1 H, naphthyl); 8.08—8.1 (m, 2 H, naphthyl). Found (%): C, 71.34; H, 3.91; N, 15.82. $C_{21}H_{14}N_4O_2$. Calculated (%): C, 71.18; H, 3.98; N, 15.81.

Synthesis of *N*-[5,7-di-*tert*-butyl-2-(het)arylbenzofuran-3-yl]furazan-3,4-diamines 44a,b (general procedure). 2,4-Di-*tert*-butylphenol (206 mg, 1 mmol) dissolved in trifluoroacetic acid (2 mL) was added with stirring to a solution of 6-(het)arylfurazano[3,4-*b*]pyrazine (1 mmol) in trifluoroacetic acid (2 mL). The reaction mixture was stored for 1 h and then diluted with water. The precipitate that formed was filtered off, washed with water several times, and recrystallized from ethanol.

***N*-(5,7-Di-*tert*-butyl-2-phenylbenzofuran-3-yl)furazan-3,4-diamine (44a).** Product **44a** was obtained as a colorless powder. The yield was 68%, m.p. 226—228 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 1.32 (s, 9 H, Bu^t); 1.54 (s, 9 H, Bu^t); 5.15 (br.s, 2 H, NH_2); 7.25 (d, 1 H, C_{arom}(H(4′)), J = 1.6 Hz); 7.28 (d, 1 H, C_{arom}(H(6′)), J = 1.6 Hz); 7.38—7.42 (m, 2 H, Ph); 7.51—7.55 (m, 1 H, Ph); 7.85—7.88 (m, 2 H, Ph); 8.25 (s, 1 H, NH). Found (%): C, 70.16; H, 6.97; N, 13.50. $C_{24}H_{28}N_4O_2$. Calculated (%): C, 71.26; H, 6.98; N, 13.85.

***N*-[5,7-Di-*tert*-butyl-2-(3-thienyl)benzofuran-3-yl]furazan-3,4-diamine (44b)** was obtained as a colorless powder. The yield was 71%, m.p. 247—250 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 1.32 (s, 9 H, Bu^t); 1.53 (s, 9 H, Bu^t); 6.15 (br.s, 2 H, NH_2); 7.23 (d, 1 H, C_{arom}(H(4′)), J = 1.6 Hz); 7.25 (d, 1 H, C_{arom}(H(6′)), J = 1.6 Hz); 7.51 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.3 Hz); 7.72—7.75 (m, 1 H, H(5″)-3-thienyl); 7.89 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz); 8.16 (s, 1 H, NH).

Found (%): C, 64.16; H, 6.97; N, 13.50. $C_{22}H_{26}N_4O_2S$. Calculated (%): C, 64.36; H, 6.38; N, 13.65.

***N*-3-[5-Methyl-7-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)-2-phenylbenzofuran-3-yl]-1,2,5-oxadiazolo-3,4-diamine (45a).** 2-Isobornyl-4-methylphenol (**24**) (244 mg, 1 mmol) dissolved in CF_3COOH (2 mL) was added with stirring to a solution of 6-phenylfurazano[3,4-*b*]pyrazine (198 mg, 1 mmol) in CF_3COOH (2 mL). The reaction mixture was stored for 1 h and then diluted with water. The precipitate that formed was filtered off, washed with water several times, and recrystallized from ethanol. Product **45a** was obtained as a colorless crystalline powder. The yield was 326 mg (74%), m.p. 214 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 0.72 (s, 3 H, CH_3); 0.85 (s, 3 H, CH_3); 0.93 (s, 3 H, CH_3); 1.39—1.45 (m, 1 H); 1.59—1.75 (m, 3 H, Alk); 2.37 (s, 3 H, CH_3); 2.41—2.44 (m, 1 H, Alk); 3.41—3.52 (m, 3 H, Alk); 6.14 (br.s, 2 H, NH_2); 7.02 (br.s, 1 H, Ar); 7.14 (br.s, 1 H, Ar); 7.38—7.42 (m, 1 H, Ph); 7.51—7.55 (m, 2 H, Ph); 7.88—7.91 (m, 2 H, Ph); 8.28 (br.s, 1 H, NH). Found (%): C, 73.02; H, 6.39; N, 12.45. $C_{27}H_{28}N_4O_2$. Calculated (%): C, 73.28; H, 6.83; N, 12.66.

Synthesis of *N*-(2-(het)arylnaphtho[2,1-*b*]furan-1-yl)furazan-3,4-diamines 46a,b (general procedure). 2-Naphthol (144 mg, 1 mmol) dissolved in CF_3COOH (2 mL) was added with stirring to a solution of 6-(het)arylfurazano[3,4-*b*]pyrazine (1 mmol) in CF_3COOH (2 mL). The reaction mixture was stored for 1 h and then diluted with water. The precipitate that formed was filtered off, washed with water several times, and recrystallized from ethanol.

***N*-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)furazan-3,4-diamine (46a).** Product **46a** was obtained as a colorless crystalline powder. The yield was 78%, m.p. 253—255 °C. ^{1}H NMR (DMSO-d_6), δ: 6.09 (s, 2 H, NH_2); 7.41—7.45 (m, 1 H, Ar); 7.51—7.58 (m, 4 H, Ar); 7.86—7.95 (m, 4 H, Ar); 8.07 (d, 1 H, Ar, J = 7.6 Hz); 8.16 (d, 1 H, Ar, J = 7.6 Hz); 8.58 (s, 1 H, NH). Found (%): C, 70.38; H, 4.17; N, 16.45. $C_{20}H_{14}N_4O_2$. Calculated (%): C, 70.17; H, 4.12; N, 16.37.

***N*-[2-(3-Thienyl)naphtho[2,1-*b*]furan-1-yl]furazan-3,4-diamine (46b)** was obtained as a colorless crystalline powder. The yield was 71%, m.p. 238—239 °C. ^{1}H NMR (DMSO-d_6), δ: 6.25 (s, 2 H, NH_2); 7.51—7.58 (m, 2 H, naphthyl); 7.61 (dd, 1 H, H(4″)-3-thienyl, J = 5.2 Hz, J = 1.2 Hz); 7.77 (dd, 1 H, H(5″)-3-thienyl, J = 5.2 Hz, J = 2.8 Hz); 7.84 (d, 1 H, naphthyl, J = 8.0 Hz); 7.90 (d, 1 H, naphthyl, J = 8.0 Hz); 8.03 (dd, 1 H, H(2″)-3-thienyl, J = 2.8 Hz, J = 1.2 Hz); 8.05 (m, 1 H, naphthyl); 8.16 (m, 1 H, naphthyl); 8.51 (s, 1 H, NH). Found (%): C, 62.15; H, 3.17; N, 16.35. $C_{18}H_{12}N_4O_2S$. Calculated (%): C, 62.06; H, 3.47; N, 16.08.

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