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Synthesis of Ditopic Ligands Containing Bis(1*H*-pyrazol-1-yl)-methane Fragments

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Abstract—New approaches have been proposed for the synthesis of compounds containing two bis(1*H*-pyrazol-1-yl)methane fragments. Nucleophilic replacement of the halogen atoms in appropriate tetrabromo derivatives by pyrazoles in the superbasic system KOH–DMSO gave ditopic chelating ligands: 1,1,2,2-tetrakis(1*H*-pyrazol-1-yl)ethane, 1,4-bis[bis(1*H*-pyrazol-1-yl)methyl]benzene, and 1,4-bis[bis(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]benzene. 1,4-Bis[bis(1*H*-pyrazol-1-yl)methyl]benzene was also synthesized by reaction of 1*H*-pyrazole with terephthalaldehyde in the presence of thionyl chloride. 1,1,2,2-Tetrakis(1*H*-pyrazol-1-yl)ethane was converted into the corresponding tetraiodo and tetranitro derivatives.

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Bis(1*H*-pyrazol-1-yl)alkanes are used as chelating ligands in coordination compounds with various metals [1]. Among these, specific interest is attracted by compounds whose molecules contain several bis(1*H*-pyrazol-1-yl)methane fragments (Fig. 1) connected through various linkers; such derivatives are multitopic chelating ligands. Ditopic ligands could give rise to homo- and heterobimetallic complexes exhibiting high catalytic and biological activity, as well as to coordination polymers [2, 3]. Supramolecular structure of such polymers may be varied by changing the linker nature; as a result, new materials, ion exchangers, molecular sieves, and sensors may be obtained [4–6].

The known synthetic approaches to ditopic pyrazole-containing ligands involve the use of unstable compounds, high temperatures, and thoroughly dehydrated solvents [4–6]. One of these is based on reaction of appropriate heterocyclic systems with dialdehyde acetals in the presence of a catalytic amount of *p*-toluenesulfonic acid. For example, prolonged heating of a mixture of malonaldehyde tetramethyl acetal and pyrazole in acid medium with continuous removal of the liberated methanol by distillation gave 1,1,3,3-tetra(1*H*-pyrazol-1-yl)propane. Compounds with a longer linker, 1,1,4,4-tetra(1*H*-pyrazol-1-yl)butane and 1,1,5,5-tetra(1*H*-pyrazol-1-yl)pentane, were synthesized in a similar way [5]. Disadvantages of this procedure are low stability of the initial acetals and long reaction time. Compounds containing two bis(1*H*-pyrazol-1-yl)methane fragments are also formed by reactions of carbonyl- and sulfinyldipyrazoles (preliminarily prepared from pyrazole potassium salt and phosgene or thionyl chloride) with various aldehydes in the presence of anhydrous cobalt(II) chloride [2, 6]. This procedure ensures high yields of the target ligands but involves some experimental difficulties related to the necessity of using alkali metals and phosgene. We can conclude that search for new methods of synthesis of compounds having two bis(1*H*-pyrazol-1-yl)methane fragments is quite important.

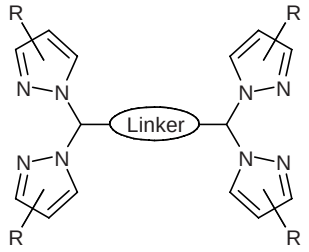
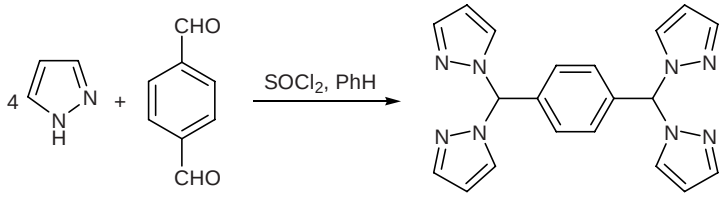


Fig. 1. Schematic representation of ditopic ligands containing bis(1*H*-pyrazol-1-yl)methane fragments.

In the present article we propose two new synthetic approaches to the above compounds. One of these is based on the reaction of the corresponding pyrazoles

Scheme 1.



Ia

with terephthalaldehyde in the presence of thionyl chloride; it was used to obtain ditopic pyrazole-containing ligands with an aromatic linker. As reported in [7], benzotriazole is capable of reacting with benzaldehyde at a ratio of 2:1 in the presence of thionyl chloride. A procedure for the preparation of (1-chloroalkyl)pyrazoles by reaction of equimolar amounts of the corresponding aldehyde and pyrazole in the presence of thionyl chloride was described in patent [8]; however, no data were given on the synthesis of bis(pyrazol-1-yl)alkanes at a pyrazole-to-aldehyde molar ratio of 2:1.

The other method involves reaction of aliphatic halogen derivatives with azoles in the superbasic system KOH–DMSO; this system was successfully used previously to effect alkylation of phenoxazine, phenothiazine [9], and aromatic amines [10], as well as double alkylation of pyrazoles with formation of bis(1*H*-pyrazol-1-yl)methanes [11].

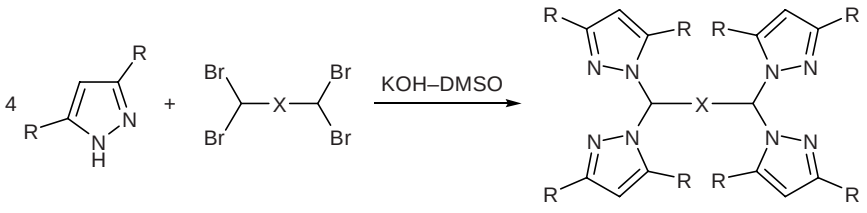
By reaction of pyrazole with terephthalaldehyde in the presence of thionyl chloride we obtained 1,4-bis[bis(1*H*-pyrazol-1-yl)methyl]benzene (**Ia**) (Scheme 1). The reaction was characterized by a short time (2 h) and good yield (71%). However, we failed to obtain 1,4-bis[bis(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]benzene (**Ib**) from 3,5-dimethylpyrazole as nucleophile; instead, 3,5-dimethylpyrazole hydrochloride was isolated. Presumably, in going from unsubstituted pyrazole to 3,5-dimethylpyrazole the stability of the product toward acids sharply decreases for steric reasons. Following the second procedure, we synthesized for the first time 1,1,2,2-tetrakis(1*H*-pyrazol-1-yl)ethane (**IIa**) by reaction of 1,1,2,2-tetrabromoethane with pyrazole in the system KOH–DMSO (Scheme 2). Our attempt to obtain in a similar way 1,1,2,2-tetrakis(3,5-dimethyl-1*H*-pyrazol-1-yl)ethane (**IIb**) resulted in isolation of only initial 3,5-dimethylpyrazole; obviously, the reason is increased steric hindrances as compared to unsubstituted pyrazole. Pyrazole and 3,5-dimethylpyrazole reacted with 1,4-bis(dibromomethyl)benzene in the system KOH–DMSO to give compound **Ia** and previously unknown derivative **Ib**, respectively (Scheme 2).

To attain high yields of the target products, it is necessary to use 1.5-fold excess of the halogen derivative, for superbasic reaction medium facilitates side processes with their participation.

To estimate the role of steric factor related to increase in the number of substituents in the pyrazole molecule, we also performed syntheses with 3(5)-methylpyrazole as nucleophile. According to the ^{1}H NMR data, the product obtained by reaction of terephthalaldehyde with 3(5)-methylpyrazole in the presence of $SOCl_2$, was a mixture of isomers (obviously, derivatives of 3- and 5-methylpyrazoles). The product was very unstable, and it decomposed on storage to form terephthalaldehyde. Likewise, isomer mixtures were formed in reactions of 3(5)-methylpyrazole with 1,1,2,2-tetrabromoethane and 1,4-bis(dibromomethyl)benzene in superbasic medium.

As follows from the signal intensity ratio for protons in positions *3* and *5* of the pyrazole rings (δ 7.44–

Scheme 2.



Ia, **Ib**, **IIa**, **IIb**

R = H (**a**), Me (**b**); **I**, X = *p*-C_6H_4; **II**, X = bond.

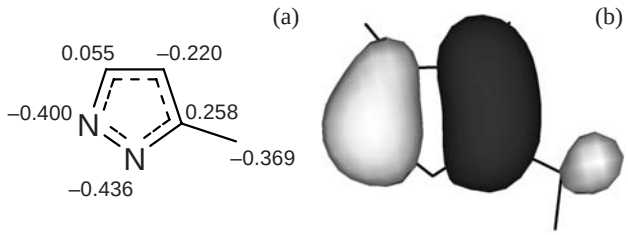


Fig. 2. (a) Charge distribution and (b) HOMO structure of 3(5)-methylpyrazolate ion according to the DFT B3LYP 6-31G** calculations.

7.39 and 7.34–7.36 ppm, respectively) in the ^{1}H NMR spectra of the products obtained by reaction of 3(5)-methylpyrazole with terephthalaldehyde, about 71% of the methyl groups occupy position *3*. The reaction in superbasic medium is characterized by a lower regioselectivity. The fraction of 3-methyl-substituted pyrazole rings in the products formed by reaction of 3(5)-methylpyrazole with 1,4-bis(dibromomethyl)benzene is 51%; in the products obtained from 1,1,2,2-tetrabromomethane, about 64% of methyl groups are attached to C^3 of the pyrazole rings.

The observed regioselectivity is consistent with the results of quantum-chemical calculations of the anion derived from 3(5)-methylpyrazole. Figure 2a shows charge distribution in 3(5)-methylpyrazolate ion. It is seen that the largest negative charge is localized on the N^2 atom; on the other hand, the highest occupied molecular orbital (HOMO) of the anion, which determines its nucleophilicity, is contributed mainly by the N^1 atom (Fig. 2b). These data led us to conclude that the reaction with terephthalaldehyde in benzene is orbital-controlled; therefore, it yields mainly 3-methyl-substituted derivatives. In going from nonpolar benzene to polar DMSO, charge control of the process becomes more significant, and the fraction of 5-methylpyrazolyl increases.

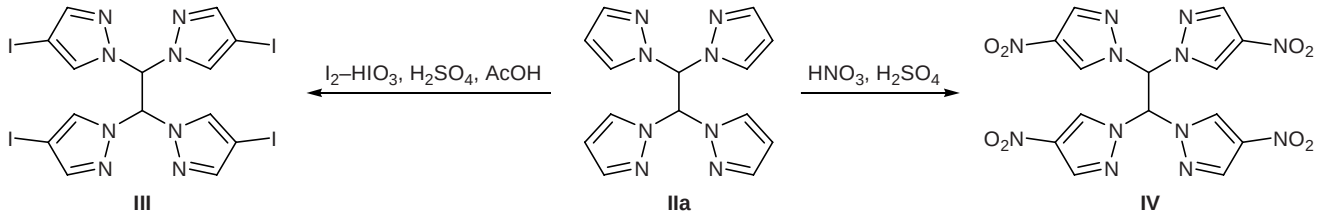
Steric factor also favors formation of 3-methylpyrazolyl derivatives. The obtained isomer ratios suggest that steric effects in superbasic medium are not so significant as in the reaction with terephthalaldehyde in the presence of thionyl chloride. Therefore, the system DMSO–KOH makes it possible to synthesize derivatives of pyrazoles having one or two methyl groups in the ring, while the reaction with terephthalaldehyde in the presence of thionyl chloride is successful only with unsubstituted pyrazole and 3(5)-methylpyrazole (no reaction occurs with 3,5-dimethylpyrazole). Thus the procedure for the synthesis of compounds containing two bis(1*H*-pyrazol-1-yl)methane fragment in superbasic medium is more general and simple; the products are readily isolated by filtration or extraction, and the procedure is more benign from the ecological viewpoint.

Coordination properties of the obtained ligands may be varied over a wide range via introduction of different substituents into the pyrazole rings. For this purpose, we were the first to synthesize tetraiodo and tetranitro derivatives of compound **IIa** (Scheme 3). It is known that *N*-alkylpyrazoles [12] and bis(1*H*-pyrazol-1-yl)methanes [13] are readily iodinated with the system I_2–HIO_3–H_2SO_4 in acetic acid. The oxidative iodination of **IIa** with I_2–HIO_3–H_2SO_4 in acetic acid at 80°C in 16 h afforded 73% of tetraiodo derivative **III**. According to the NMR data, electrophilic replacement of hydrogen in the pyrazole ring by iodine occurred with complete regioselectivity at the C^4 atom of the pyrazole rings, which possesses the largest electron density. The nitration of compound **IIa** was performed using a mixture of nitric and sulfuric acids at a molar ratio of 1:5.5, by analogy with the procedure for nitration of bis(1*H*-pyrazol-1-yl)methanes [14]. As in the iodination, the nitro group entered exclusively the 4-position of the pyrazole rings. The obtained iodo and nitro derivatives **III** and **IV** are characterized by poor solubility in most organic solvents and enhanced thermal stability (according to the data of thermogravimetric analysis, they melt with decomposition at 349 and 388°C, respectively).

EXPERIMENTAL

The NMR spectra were recorded on a Bruker AV-300 spectrometer. The IR spectra were measured on a Specord 71IR spectrometer. Mass spectrometric and

Scheme 3.



thermogravimetric analyses of compounds **III** and **IV** were performed on TRACE DSQ (Thermo Electron Corporation, USA) and SDT Q600 instruments (TA Instruments, USA) at the Analytical Center of the Tomsk Polytechnic Universitety. The progress of reactions and the purity of products were monitored by TLC on Silufol plates using benzene–acetone (3:2) as eluent; development with iodine vapor.

1,4-Bis(dibromomethyl)benzene was synthesized according to the procedure described in [15]. Dimethyl sulfoxide was kept for 24 h over pelleted KOH and distilled under reduced pressure. Thionyl chloride was distilled just before use. The other reagents were commercially available products which were used without additional purification.

Nonempirical calculations were performed using HyperChem for Windows [16]. Initial structures for optimization of geometric parameters were simulated by the PM3 method. Geometry optimization was performed using 6-31G* basis set for isolated ions by the conjugate gradient method until a mean-square gradient of less than 10 cal $Å^{-1}$ mol^{-1} was reached. The optimized structures were calculated in terms of the DFT UHF approximation (6-31G** basis set, B3LYP combination potential).

1,4-Bis[bis(1*H*-pyrazol-1-yl)methyl]benzene (Ia). *a*. A mixture of 2 g (29.4 mmol) of pyrazole, 3.29 g (58.8 mmol) of finely powdered potassium hydroxide, and 10 ml of DMSO was stirred for 2 h at 80°C. A solution of 3.13 g (7.35 mmol) of 1,4-bis(dibromomethyl)benzene in 15 ml of DMSO was added dropwise, the mixture was stirred for 21 h at 80°C, diluted with 200 ml of water, and neutralized with hydrochloric acid, and the precipitate was filtered off. Yield 1.439 g (53%), light yellow crystals, mp 168–169°C (from EtOH); published data [2]: mp 165–166°C. IR spectrum, ν, cm^{-1}: 1500, 1330, 1020 (pyrazole); 1610 (C=C_{arom}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.33 d.d (4H, 4-H, J = 0.3, 2.3 Hz), 7.05 s (4H, H_{arom}), 7.54 d (4H, 3-H, J_1 = 2.3, J_2 = 0.6 Hz), 7.62 d (4H, 5-H, J = 1.7 Hz), 7.72 s (2H, NCHN). Found, %: C 64.46; H 4.62; N 30.45. $C_{20}H_{18}N_8$. Calculated, %: C 64.85; H 4.90; N 30.25.

b. Thionyl chloride, 3.55 g (29.8 mmol), was slowly added on cooling with ice to a mixture of 1 g (14.9 mmol) of pyrazole, 0.5 g (3.73 mmol) of terephthalaldehyde, and 5 ml of benzene. The mixture was heated for 2 h under reflux and poured into 150 ml of hexane, and the precipitate was filtered off and dried under reduced pressure (20 mm). Yield 0.973 g (71%). The spectral parameters of samples of **Ia** obtained as described in *a* and *b* were identical.

1,4-Bis[bis(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]benzene (Ib) was synthesized as described above for compound **Ia** (method *a*) from 2 g (20.8 mmol) of 3,5-dimethylpyrazole, 2.33 g (41.7 mmol) of KOH, and 2.22 g 5.21 mmol) of 1,4-bis(dibromomethyl)benzene; reaction time 24 h. Yield 1.49 g (60%), light yellow needles, mp 224.5–226°C (from benzene). IR spectrum, ν, cm^{-1}: 1540, 1500, 1330, 1010 (pyrazole). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.09 s (12H, 3-CH_3), 2.13 s (12H, 5-CH_3), 5.90 s (4H, 4-H), 6.99 s (4H, H_{arom}), 7.70 s (2H, CH). Found, %: C 70.01; H 7.10; N 22.90. $C_{28}H_{34}N_8$. Calculated, %: C 69.68; H 7.10; N 23.22.

1,1,2,2-Tetrakis(1*H*-pyrazol-1-yl)ethane (IIa). A mixture of 1 g (14.7 mmol) of finely powdered potassium hydroxide and 10 ml of DMSO was heated to 80°C under vigorous stirring. After 30 min, a solution of 1.29 g (3.68 mmol) of 1,1,2,2-tetrabromoethane in 10 ml of DMSO was added dropwise to the resulting suspension, the mixture was heated for 5 h at 80°C and diluted with 200 ml of water, and the precipitate was filtered off and dried (0.15 g). The filtrate was treated with chloroform (5×15 ml), the extract was washed with water (4×10 ml) and dried over calcium chloride, and the solvent was distilled off to obtain an additional portion (0.468 g) of compound **IIa**. Overall yield 0.618 g (57%), colorless crystals, mp 271–273°C. IR spectrum, ν, cm^{-1}: 1521, 1437, 1310, 1051 (pyrazole). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.13 t (4H, 4-H, J = 2 Hz), 7.47 d (4H, 3-H, J = 2 Hz), 7.65 d (4H, 5-H, J = 2 Hz), 7.83 s (2H, NCHN). Found, %: C 56.84; H 4.48; N 38.07. $C_{14}H_{14}N_8$. Calculated, %: C 57.13; H 4.79; N 38.29.

Reaction of 3(5)-methylpyrazole with terephthalaldehyde. Thionyl chloride, 3.55 g (29.84 mmol), was added dropwise on cooling to a solution of 1.223 g (14.92 mmol) of 3(5)-methylpyrazole and 0.5 g (3.37 mmol) of terephthalaldehyde in 5 ml of benzene. The mixture was heated for 2 h under reflux, excess thionyl chloride was removed by repeated distillation each time with addition of toluene (5×2 ml). The remaining solution was diluted with hexane, and the precipitate was filtered off, washed with 20% aqueous ammonia, and dried in a vacuum desiccator over KOH. Yield 1.16 g (81%) (mixture of 3- and 5-methyl derivatives). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27–2.38 (12H, 3-CH_3, 5-CH_3), 6.96–6.99 (4H, H_{arom}), 7.34–7.36 (2.84H, 5-H), 7.44–7.49 (1.16H, 3-H), 7.53–7.57 (2H, CH).

Reaction of 3(5)-methylpyrazole with 1,1,2,2-tetrabromoethane. The reaction of 1 g (12.20 mmol) of 3(5)-methylpyrazole with 1.067 g (3.05 mmol) of 1,1,2,2-tetrabromoethane was carried out as described above for the synthesis of compound **IIa**; the reaction mixture was heated for 91 h at 80°C. Yield 0.51 g (57%) (mixture of 3- and 5-methyl derivatives). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.14–2.38 (12H, 3-CH_3, 5-CH_3), 7.37 (1.45H, 3-H), 7.51–7.53 (2H, CH), 7.57–7.72 (2.55H, 5-H).

Reaction of 3(5)-methylpyrazole with 1,4-bis-(dibromomethyl)benzene. The reaction of 1 g (12.20 mmol) of 3(5)-methylpyrazole with 1.624 g (3.812 mmol) of 1,4-bis(dibromomethyl)benzene was carried out as described above for the synthesis of compound **IIa**; the reaction mixture was heated for 68 h at 50°C. Yield 0.86 g (53%) (mixture of 3- and 5-methyl derivatives). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.27–2.38 (12H, 3-CH_3, 5-CH_3), 6.94–7.00 (4H, H_{arom}), 7.34–7.37 (2.04H, 5-H), 7.44–7.49 (1.96H, 3-H), 7.53–7.57 (2H, CH).

1,1,2,2-Tetrakis(4-iodo-1*H*-pyrazol-1-yl)ethane (III). A suspension prepared from 0.082 g (0.279 mmol) of compound **IIa**, 0.113 g (0.446 mol) of iodine, 0.039 g (0.223 mmol) of iodic acid, 0.1 ml of 30% sulfuric acid, and 1 ml of acetic acid was stirred for 6 h at 80°C (until the iodine color disappeared). The mixture was diluted with 20 ml of water, and the precipitate was filtered off, repeatedly washed with a solution of KI and with water, and dried under reduced pressure (20 mm). Yield 0.163 g (73%), colorless crystals, mp 349°C (decomp., from DMF). ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 8.05 s (4H, 3-H), 8.44 s (4H, 5-H), 8.47 s (2H, CH). Mass spectrum, m/z (I_{rel}, %): 798 (1) $[M]^+$, 413 (24) $[M - 2Pz(I)]^+$, 399 (100) $[M - (PzI)_2CH]^+$, 273 (93) $[M - (PzI)_2CH - I]^+$, 194 (33) $[Pz(I)H]^+$. Found, %: C 20.74; H 1.31; N 13.90. $C_{14}H_{10}I_4N_8$. Calculated, %: C 21.07; H 1.26; N 14.04.

1,1,2,2-Tetrakis(4-nitro-1*H*-pyrazol-1-yl)ethane (IV). A mixture of 0.29 g (1.00 mmol) of compound **IIa**, 1.3 ml of 68% nitric acid (20.0 mmol of HNO_3), and 6 ml of 98% sulfuric acid was kept for 24 h at room temperature. The mixture was then diluted with an ice–water mixture and neutralized with sodium carbonate. The precipitate was filtered off, washed with water, and dried under reduced pressure (20 mm). Yield 0.33 g (81%), colorless crystals, mp 388°C (decomp.; from DMF–water, 5:2). ^{1}H NMR spectrum (DMF-d_7), δ, ppm: 8.46 s (4H, 3-H), 8.95 s (2H, CH), 9.38 s (4H, 5-H). Mass spectrum, m/z (I_{rel}, %): 361 (4) $[M - Pz(NO_2)H]^+$, 251 (13) $[M - 2Pz(NO_2)]^+$, 237 (100) $[M - (Pz(NO_2))_2CH]^+$, 191 (18) $[M - 2Pz(NO_2) - NO_2 - H]^+$, 113 (38) $[Pz(NO_2)H]^+$. Found, %: C 35.72; H 2.30; N 35.85. $C_{14}H_{10}N_{12}O_8$. Calculated, %: C 35.45; H 2.13; N 35.44.

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