Cyclocondensation of 2-Hydroxyimino-1-(naphthalen-1-yl)butane-1,3-dione with Alkyl Hydrazines Leading to Substituted 4-Nitrosopyrazoles

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Abstract: Cyclocondensation of 2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione with alkyl hydrazines leading to new 1-alkyl-3(5)-methyl-5(3)-(naphthalene-1-yl)-4-nitrosopyrazolesis described. 8 previously unknown N-alkyl-4-nitrosopyrazoles with a 1-naphthalene substituent at the 3 or 5 position of the pyrazole ring were obtained as a result. It was found that yields of naphthyl-substituted pyrazoles with N-alkyl groups near the naphthalene substituent were significantly lower than for 3-(naphthalen-1-yl)-substituted pyrazoles.Particular yields of pairwise formed isomeric nitrosopyrazoles were associated the with different electrophilicity of the two carbonyl groups of the initial diketone. Using quantum chemical calculations by the DFT method B3LYP-D3/6-311G(d,p), the potential energies of the various conformers were estimated to draw a conclusion about the preferred attack of alkyl hydrazine on the carbonyl group, associated with the naphthalene ring. ^{1}H NMR and 2D ^{1}H-^{13}C HSQCspectra of the compounds confirmed this direction of the reaction. The crystal structures of the synthesized compounds were established by X-ray powder diffraction technique. Crystal structure data were in agreement with quantum chemical calculations.

Introduction

The prevalence of pyrazole cores in biologically active molecules causes the sustained interest of chemists to this class of heterocyclic compounds.[1-4] Pyrazole derivatives are used as agrochemicals, acaricides, fungicides, herbicides, pharmaceuticals, etc.[5-8]The nonsteroidal anti-inflammatory drug Celecoxib is one of the best-known examples.Biologically active pyrazoles of natural origin are known.[9] Moreover, compounds containing the pyrazole core bonded to the naphthalene ring are exhibited the biological activity often.

So, in the paper[10] the biological activity of compounds containing pyrazole, thiazole, and naphthalene rings was studied. It was revealed that the presence of a naphthalene ring enhances the antitumor activity of such compounds. The synthesis and pharmacological activity of N-arylpyrazoles as strong σ1 receptor antagonists was reported inarticle.[11] The according N-naphthyl derivative is selected as a candidate for clinical trials by the authors.

Naphthalene substituted pyrazolines having activity in the treatment of diabetes have been described.[12] It became known that some naphthyl and hetaryl substituted pyrazolines are antidepressants.[13] Palladium (II) complexes bearing 4-nitropyrazole-based Schiff base ligands exhibit high cytotoxic activity exceeding the activity of cisplatin.[14]Inarticles[15, 16] the authors described antitumor activity in polyphenols containing a naphthylpyrazoline skeleton. 4-substituted N-phenyl-3-(4-fluorophenyl)- and 3-(4-chlorophenyl)-pyrazoles exhibit antitubercular activity.[17,18]

Nitroso derivatives and amino derivatives of pyrazoles exhibit biological activity very often. The synthesis of tuberculostatically active 3-trifluoromethyl-5-phenyl-substituted nitrosopyrazoles was described.[19]The article[20]describes the creation of ultrashort antimicrobial peptidomimetics based on 4-amino-1H-pyrazole-3-carboxylic acid methyl ester. A series of anti-cancer active pyrazole derivatives with amide substituents in position 4 of the pyrazole ring were obtained.[21] The authors of article [22] reported that ethyl 4-amino-1H-pyrazole-3-carboxylic acid might be a potential anti-cancer agent. 1,3-diphenylpyrazoles with various amide substituents in the 4-position of the pyrazole ring are exhibit cytotoxic activity.[23] The review[6] reported antimicrobial and antifungal activity in some mono-, di- and trisubstituted 4-nitrosopyrazoles, as well as the anticonvulsant effect of 5-aryl-substituted 4-nitro- or 4-halogenpyrazoles. New antimycobacterial agents were synthesized based on 4-amino-3-trifluoromethyl-5-phenyl-1H-pyrazole.[24]

Based on the foregoing, it can be concluded that pyrazole derivatives with nitrogen-containing functions in the position 4 of the cycle are of great interest to the scientific community. They are widely used for the synthesis of various biologically active

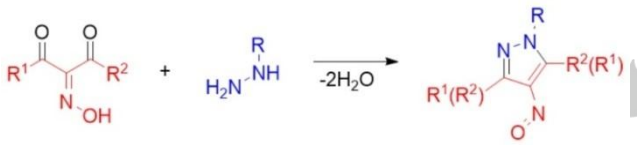
substances and themselves directly have increased biological activity. The insertion of a naphthalene core in such molecules often has a positive effect on their beneficial properties.

Therefore, in this work we synthesized previously unknown N-alkyl-4-nitrosopyrazoles with a naphthalene core. The reaction of 2-hydroxyimino-1,3-diketones with hydrazines is the most convenient approach for the synthesis of 4-nitrosopyrazoles of various structures. Also, the influence of the starting 2-hydroxyimino-1,3-diketones structure on direction of this heterocyclization is poorly understood.

The structure of the starting 2-hydroxyimino-1,3-diketone and the obtained isomeric nitrosopyrazoles were determined using quantum chemical calculations and was confirmed by 1D and 2D NMR spectroscopy, X-ray powder diffraction, IR-, UV-Vis spectroscopy and chromato-mass spectrometry.

Results and Discussion

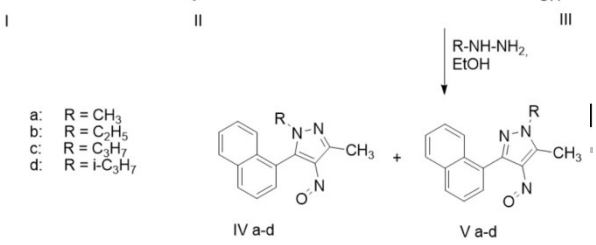
Cyclocondensation of mono-substituted hydrazines with asymmetric 2-hydroxyimino-1,3-diketones leads to a mixture of regioisomeric 4-nitrosopyrazoles with different ratio (see Scheme 1).[25]



Scheme 1. Cyclocondensation of mono-substituted hydrazines with asymmetric 2-hydroxyimino-1,3-diketones.

The synthesis of new N-alkyl-substituted nitrosopyrazole derivatives with aryl and methoxymethyl substituents in 3 or 5 positions was reported earlier.[26] The interaction of 2-(hydroxyimino)-4-methoxy-1-(naphthalen-1-yl)butane-1,3-dione with alkylhydrazines leaded to the formation of sole 5-(naphthalen-1-yl)-substituted regioisomer of 4-nitrosopyrazoles, due to the influence of substituents.

In this paper the results cyclocondensation of *2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione***III** with some alkyl-substituted hydrazines in ethanol are reported for the first time. Two regioisomeric 4-nitrosopyrazoles with 4 alkylhydrazines were formed as blue thick oil (**IVa-c**), blue solid (**IVd**), or blue-green crystals (**Va-d**) (see Scheme 2).



Scheme 2. Cyclocondensation of mono-substituted hydrazines with 2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione.

The experimental results was exhibited that the yield of 5-(naphthalen-1-yl)-substituted isomers **IVa-d** for all N-alkyl groups was significantly lower than for 3-(naphthalen-1-yl)- substituted compounds **V a-d** (see Table 1).

Table 1. Reaction Products Yields.

Compounds **IV**	Isolated yield, %	Compounds **V**	Isolated yield, %
IV a	4	V a	42
IV b	14	V b	46
IV c	8	V c	53
IV d	22	V d	46

The structures of the obtained regioisomeric nitrosopyrazoles were investigated using by ^{1}H NMR, ^{13}C NMR spectroscopy, 2D ^{1}H-^{13}C HSQC experiments, X-ray powder diffraction, IR-, UV-Vis spectroscopy and chromato-mass spectrometry.

In accordance with the literature.[25b] the nitroso-group in all studied compounds provides a strong band at 1325-1346 cm^{-1} The n→π* bands of the nitroso-group presents at 680-685 nm in the UV-Vis spectrum of **IV a-d** and **V a-d**.

NMR spectra were recorded in [D6]DMSO or $CDCl_3$ at 298 K. Analysis of ^{13}C NMR spectra of the nitrosopyrazoles **IV-V** showed that methyl carbon atoms C3-CH_3 in the **IV**-isomers and C5-CH_3 in the **V**-isomers resonated at 13.10-13.42 ppm and at 9.9-22.5ppm, respectively. Nuclei of aliphatic carbons adjacent to the N1 pyrazole nitrogen resonated at 35.98-51.06 ppm. In agreement with the literature [25b] pyrazole ring C4 nucleus resonated at 159.91-161.37 ppm.

^{1}H NMR spectra of compounds **IV-V** displayed C3(5)-CH_3 protons resonating as a broadened singlets at 2.36-2.48 ppm (**IV a-d**) and at 2.80-2.84 ppm (**V a-d**). Aromatic protons for all the studied compounds resonated at 7.04-8.25 ppm.Protons of N-alkyl substituents for compounds **V a-d** resonated at0.97-4.67ppm region.

^{1}H NMR spectrum of **V d** exhibited one doublet at 1.66 ppm for six equivalent $(CH_3)_2$ protons and septet at 4.67 ppm for CH-group. However, bulky naphthalene substituent inregioisomer **IV d** provides non-equivalence of CH_3–groups.These protons resonated as two doublets at 1.45-1.48 ppm.

Analysis of ^{1}H NMR spectra of compounds **IV b** or **IV c** showed non-equivalence of N-CH_2-group protons.We have found that the H_A and H_B proton signals were cleanly separated with the chemical shifts difference between $H_A/H_B\Delta\delta$=51.35 Hz (0.086 ppm) for **IV b**and $\Delta\delta$=101.46 Hz (0.169 ppm) for **IV c** (Figure 1). Spin-spin splitting for N-CH_2-group protons indicated coupling each proton to the geminal and vicinal protons to give the observed multiplet.

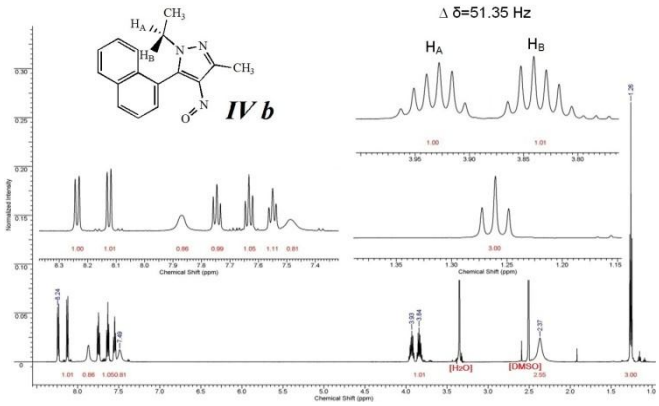


Figure 1.[1]H NMR spectrum of 1-ethyl-3-methyl-5-(naphthalen-1-yl)-4-nitroso-1H-pyrazole.

The 2D ^{1}H-^{13}C HSQC experiment showed a correlation of non-equivalent protons signals with the methylene group carbon atom signal (Figure 2).

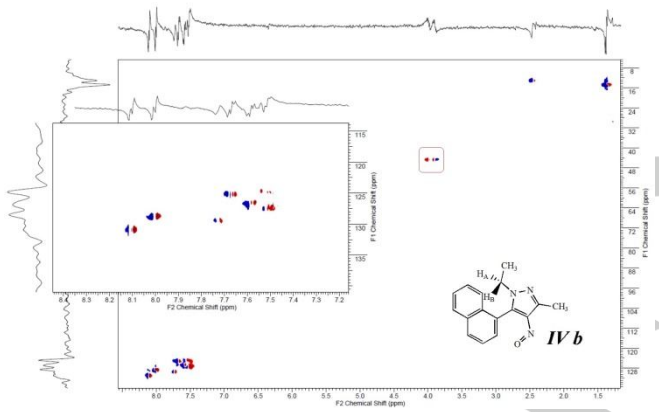


Figure 2.2D ^{1}H-^{13}C HSQC spectrum of 1-ethyl-3-methyl-5-(naphthalen-1-yl)-4-nitroso-1H-pyrazole.

^{1}H NMR spectrum (DMSO-d6) of **Vb** displayed all the corresponding proton signals of the molecule with a characteristic spin-spincoupling (Figure 3), δ, ppm: 7.44-8.07 (m, 7H, Ar-H), 4.30 (q,2H, CH_2-CH_3), 2.84 (br s, 3H, CH_3), 1.47 (t,3H, CH_2-CH_3).

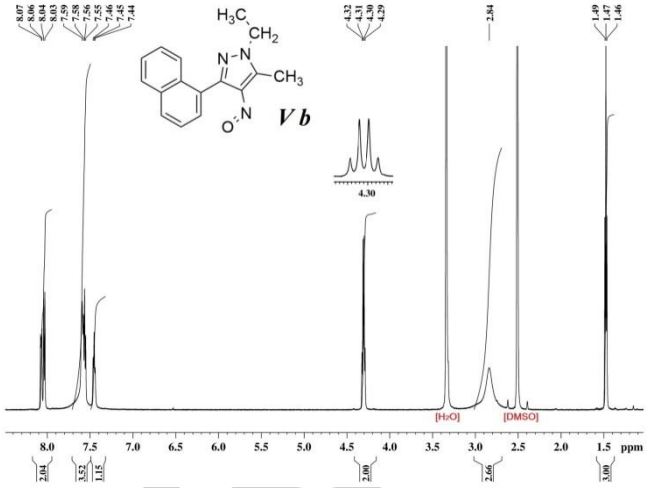


Figure 3.[1]H NMR spectrum of 1-ethyl-5-methyl-3-(naphthalen-1-yl)-4-nitroso-1H-pyrazole.

Thus, ^{1}H NMR spectroscopy data of the liquid regioisomers **IV** confirmed the presence of the naphthalene substituent at position 3 of the pyrazole ring, and the solid regioisomers **V** at position 5, as shown in Scheme 2.

Evidently, higher yields of compounds **V** compared to **IV** can be explained by the different reactivity of carbonyl groups in 2-hydroxyimino-1,3-diketone **III** in relation to nucleophilic reagents - alkylhydrazines.

Quantum-chemical calculations of the geometrical and electron structures of the different conformers of the *2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione***III** molecule were carried out by DFT B3LYP-D3/6-311G(d,p) method[27-31]with use of ORCA 4.0 software[32, 33] to compare the electrophilicity of carbonyl groups at C3 and C5 atoms (Figure 3) and their reactivity in the nucleophilic addition reactions.

The electrophilic centers, more suitable for nucleophilic attack, were determined with help of the condensed Fukui functions f^{+} of every atom, calculated as $f^{+} = q_N - q_{N+1}$. Herein q_N and q_{N+1} are the effective charges of specific atom of neutral molecule and, correspondingly, molecule, containing one additional electron.[34] These charges were estimated by the method of natural population analysis (NPA),[35] realized in JANPA 2.02 software.[36, 37]

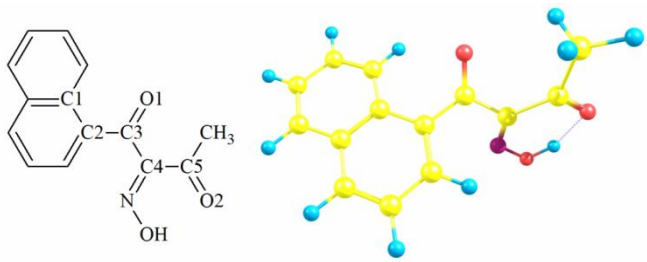


Figure 4. Structural formula of the2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione molecule (left), structure of its most stable conformer (right)

Geometry optimization was performed in the case of neutral compounds. These geometries were used without any changes

for calculation of electron structures of molecule with one additional electron. All calculations were carried out in the frame of spin-unrestricted Kohn-Sham method (UKS).

As the result of performed simulations it was shown that geometrical structure of the *2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione***III**compound could be presented by 14 diastereomers, distinguishing by the values of the different torsion angles (Figure 4, Table 2). Excluding conformers 4 and 10, the angles between the plane formed by C1, C2, C3 atoms and the plane crossing C2, C3, O1 atoms were in the range 26º to 56º. It indicated a distortion of conjugated *π*-electron system of naphthyl group and its adjacent carbonyl group that made the C3 atom reactive for nucleophilic attack.

Comparing the values of the condensed Fukui functions of C3 and C5 atoms it should be noted that in the most cases, excluding conformers 1 and 3, electrophilic properties were mostly pronounced for C3 atom. More than half of diastereomers had the f^+(C3) values a few times larger than f^+(C5).

Thus, according to a number of factors, it should be concluded that the probability of nucleophilic addition to the carbon atom C3 of carbonyl group connected with 1-naphthyl substitute in the *2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione* **III** molecule was higher than to C5 - the carbon atom of the "aliphatic" carbonyl group, sited faraway from the naphthalene cycle.

Table 2. Parameters of 2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione molecule conformers.

Conformer	RTE[a], kJ/mol	Torsion angles, degrees			$f^+(C_3)$	$f^+(C_5)$
		$C_1C_2C_3O_1$	$C_2C_3C_4C_5$	$C_3C_4C_5O_2$		
1	0.00	26.1	-144.8	-172.2	0.069	0.069
2	5.05	-134.8	24.8	22.4	0.143	0.010
3	5.48	135.5	157.3	174.2	0.068	0.087
4	5.61	-2.6	-95.0	11.6	0.080	0.043
5	6.52	34.7	35.6	15.9	0.150	0.010
6	15.11	-27.4	147.5	-84.9	0.137	-0.017
7	15.66	151.4	-69.1	-0.1	0.069	0.055
8	15.79	152.2	122.7	-25.1	0.085	0.042
9	16.06	-138.2	-145.2	80.6	0.140	-0.015
10	19.29	3.9	-102.8	169.8	0.114	0.013
11	22.00	37.4	-176.8	-95.1	0.147	-0.021
12	27.76	123.7	179.0	98.3	0.152	-0.023
13	29.54	147.3	-45.1	-28.4	0.057	0.052
14	29.92	146.6	129.7	-29.6	0.114	0.011

[a] RTE – relative total energy, i.e. the total energy of the corresponding conformer relative to the total energy of the most stable one from them

The crystal structures of condensation products of 2-(*hydroxyimino*)-1-(*naphthalen*-1-*yl*)*butane*-1,3-*dione* **III** with various alkylhydrazines were investigated to answer the question concerning the initial condensation center. The condensation starting with the attack on the first ketone group obviously generates a product with the naphthyl localization in the 3rd position of the pyrazole ring. When attacking the second ketone group, the naphthyl is in the fifth position of pyrazole.

The crystal structure investigation has been carried out using X-ray powder diffraction technique. Difficulties in obtaining single crystal samples are the characteristic of the compounds under investigation. The substances have been prepared in the form of a thin crystalline powder and were not suitable for the application of the classical single crystal method. There were no preliminary structural analogues or prototypes of the structures at the beginning of the studies.[38] The investigations based on the similarity of powder diffraction patterns[39] have not given any suggestions. The structural study have included all the necessary steps namely: X-Ray powder patterns scanning, indexing and cell parameters determination, Space Group selection, the atomic model preparation and the crystal structure refinement. The Simulated annealing approach (Monte Carlo method) was used as the main technique for the structure modeling in direct space. Recently the technique has shown high efficiency for structures constructed mainly from known molecular fragments.[40*a*, 40*b*, 40*c*]The Table 3 presents the obtained crystal structure data and experimental conditions. The molecular structures and unit cell parking are depicted in Figure 5. The crystal structure data were deposited in CSD 1975806-1975808, 1976877.

Table 3. Crystallographic parameters and experimental details of X-ray powder diffraction investigation for **Va-d**.

Chemical formula	$C_{15}H_{13}N_3O$**Va**	$C_{16}H_{15}N_3O$**Vb**	$C_{17}H_{17}N_3O$**Vc**	$C_{17}H_{17}N_3O$**Vd**
Molecular weight	**251,283**	**265,310**	**279,336**	**279,336**
Space group	P 2_1/n	P $2_12_12_1$	P $2_12_12_1$	P 2_1ca
a, Å	13.683(1)	14.533(1)	14.594(1)	11.805(1)
b, Å	9.268(1)	11,223(1)	12.325(1)	11.428(1)
c, Å	11.112(1)	8.673(1)	8.358(1)	11.269(1)
α, (°)	90.0	90.0	90.0	90.0
β, (°)	109.97(1)	90.0	90.0	90.0
γ, (°)	90.0	90.0	90.0	90.0
$V_{un.cell}$, $Å^3$	1324.38	1414.70	1503.32	1520.43
Z	4	4	4	4
V/Z, $Å^3$	331.09	353.67	375.83	380.11
$\rho_{calc.}$, g/cm^3	1.260	1,246	1.234	1.234
$V_{mol, Hirshfeld}$	325.31	346.62	368.20	372.47
$S_{mol\ Hirshfeld}$	296.53	320.42	345.86	336.41
TorsAngel(C-C-N-N)	111.6	-68.6	-68.8	-50.6
Aspherisity	0.127	0.143	0.116	0.092
T, K	295	295	295	295
Diffractometer	X´PertPRO	X´PertPRO	X´PertPRO	X´PertPRO
Radiation *λ, Å*	CuKα λ_1= 1.54056, λ_2= 1.54439	CuKα λ_1= 1,54056, λ_2= 1,54439	CuKα λ_1= 1.54056, λ_2=1.54439	CuKα λ_1= 1.54056, λ_2= 1.54439
Scan. area,2θ (°)	3.039–90.935	3,013-90,909	3,013-90,909	3,013-90,909
Num.of points	3380	3380	3380	3380
Num. of refl.	311	272	291	281
R_p, %	6.8	6,7	5.3	6.3
R_{wp}, %	9.8	8,6	7.6	9.1
R_{exp}, %	5.3	3,8	4.8	4.6

$S = R_{wp} / R_{exp}$	1.85	2,24	1.57	1.9

It turned out that in all cases the naphthyl substituent was in the third position of pyrazole ring. It means that condensation started at the ketone group at C_3. To be sure in relative orientation of the alkyl and naphthyl substituents in pyrazole ring the simulation of possible cases were carried out. It should be taken into consideration that small difference between carbon and nitrogen could be compensated by distortions of other parts of the structure. The structure **Va** was the most tolerant to the displacement of the substituents. The structure refinement with new configuration has led to *R*-factor larger on 1.5%, which, however, was accompanied by some unacceptable distortions of interatomic distances. For other structures, the simulation finished with unacceptable convergence of neighboring molecules in the unit cell parking that excluded their existence.

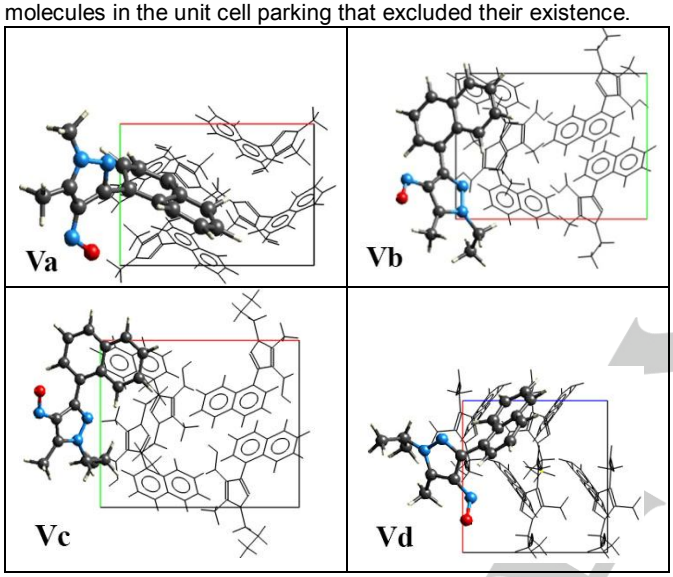


Figure5. Molecular structures of nitrosopyrazoles Va-d.

According to the data given in Table 3, the specific molecule volume increases in good accordance with composition. A modification molecule composition on methyl group results in approximately 20 Å^3 of molecular volume increasing. Replacement of the n-propyl by iso-propyl group causes volume increasing on ~5 Å^3, due to the less flexible structure of the substituent. It is substance characteristic that the density of the remains approximately at the same range with the substituent increasing (Table 3). A very moderate change in molecule volume is in significant contrast to the observed changes in the way of molecule packing in the crystal lattice. The absence of similarity in the molecule packing correlated with the absence of a certain similarity of the X-ray of diffraction patterns of the compounds under consideration (Figure 5). This indicates different orientation of the largest fragments in the structure. As a consequence, the differences in the Space Groups of the structures are observed (Table 3).

Taking into account the range of the *torsion angle TA* (*C-C-A-A)* variation characterizing the angle between the planes of pyrazole ring and naphthyl-group (Table 3), the compounds can be divided into two groups. The first includes **Va**, in which the hydrazine fragment (*N-N*) in pyrazole ring is oriented above the plane of the naphthyl-substituent (Figure 5). The second group includes compounds **Vb-d**, where (*N-N*) is under the plane (negative torsion angle). However, if we abstract the individuality of the substituents in **Va**, the torsion angle will be 68.4^o, which is very close to the phases **Vb** and **Vc** (Δ=0.4^o) (Table 3). In general, the angular range between the plane of the pyrazole ring and the naphthyl-group is in the limited range of 50-70^o. Despite the fact that the compound compositions are very close (18 of the 19-21 non-hydrogen atoms) and includes two very rigid structural fragments (pyrazole ring and naphthalene), there are significant differences in the geometry of the molecule packaging.

Projections of the structure on the large face of the unit cell are shown in Figure 5. The main distinctive feature of the molecule packing is the lack of influence of the main structural blocks on their relative arrangement, as well as the lack of intermolecular H-bonds. When packing, the geometry of large blocks does not cause special restrictions, and the molecule, as a whole, remains as a rigid particle. The relatively low specific density of the products indicates a low density of molecule packing with low asymmetry. Some similarity of the packing is seen only for the phases **Vb** and **Vc** (Figure 5). It can be assumed that the considered structural features of substituents in the pyrazole ring are important for the chemical activity of substances.

Thus, the structural study shows that crystalline products of condensation are formed as a result of alkylhydrazine attack on the first ketone group of *2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione* **III**. It can be assumed that the difficulty in crystallization of isomeric products seems to be related to the geometric shape of molecules with increased sphericity, which contributes to the disorientation of molecules and the lack of translational symmetry.

Conclusion

Studying the reaction of 2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione with alkylhydrazines showed that in all cases substituted nitrosopyrazoles **Va-d** with alkyl substituents at the nitrogen atom remoted from the α-naphthalene substituent in nitrosopyrazole formed with high yields. The yield of nitrosopyrazoles **IVa-d** with alkyl substituents at the nitrogen atom located closer to the α-naphthalene substituent was several times lower. Quantum chemical calculations by DFT B3LYP-D3 / 6-311G (d, p) method with use of ORCA 4.0 software showed that the reason for this direction of the reaction was due to the higher electrophilicity of the carbon atom of the carbonyl group associated with naphthalene. All substituted nitrosopyrazoles were synthesized for the first time, isomers IV and V were separated on a chromatographic column. The structure of substituted nitrosopyrazoles was confirmed by NMR spectroscopy and X-ray powder diffraction data.The pattern of N-substituent protons spin-spin splitting can be used as a reliable indicator to differentiate between regioisimers of substituted N-alkylpyrazoles.

Experimental Section

X-Ray powder diffraction analysis

The structure determinations were carried out with the application of X-ray powder diffraction technique. The experimental data were collected using X'Pert Pro (PANalytical) diffractometer equipped with a secondary flat graphite monochromator in conjunction with PIXel semiconductor detector. $Cu_{K\alpha}$ radiation was used (kα1 = 1.54056 Å, kα2 = 1.54439 Å). The samples were prepared using a standard holder by top-loading. The excess substance was cut by the fine grained substance. The diffraction pattern was scanned with the step of 0.013_ in 2Θ and counting time of 55 s/step in the most informative angular range from 9_ to 90 in 2Θ at room temperature.

Cell parameters were obtained from d-spacing by indexing and refining using programs described inarticles.[41,42]The space group was determined from the analysis of systematic absences. The structure solutions were obtained using methods "in direct space" adapted to powder diffraction data (FOX program).[43-45] H-atoms were included into the refined structure models and rigidly connected to their C and N atoms using molecular graphic package[46] with d(N–H) = 0.90 A and d(C–H) = 0.96 A and U_{iso}(H) = 0.152 A2. The final refinement was carried out by Rietveld method.[47]

^{1}H NMR spectra and ^{13}C NMR spectra were run on a Bruker Avance III 600 spectrometer using tetramethylsilane (TMS) as an internal standard at 600.13 and 150.90 MHz, respectively.Assignments of ^{1}H, ^{13}C were determined by analysis of chemical shifts and assisted by 2D ^{1}H-^{13}C HSQC experiments.

The UV-Vis spectra were recorded on a HELIOS OMEGA spectrophotometer in 1 cm quartz cuvettes at a concentration of 1×10^{-4} mol / L for 200 - 400 nm and a concentration of 1×10^{-2} mol / L for 400 - 800 nm in ethanol.

Mass spectra of compounds **IVd**, **Va-d** were recorded on a Finnigan MAT 8200 instrument. The HPLS/MS spectra of compounds **IVa-c** were recorded on a Shimadzu LC/MS-2020 instrument using a RAPTOR ARC-18 (100) column.

Elemental analyses were performed on an Analytischer Funktiontest vario El II Fabinstrument.

Infrared spectra were measured using a Nicolet Impact 400 FTIR spectrometer equipped with a SpecTRA TECH Inspect IR microscope.

All commercial reagents were used without further purification. 1-(naphthalen-1-yl)butane-1,3-dione **II** was prepared according to literature procedure.[48] Nitrosation of **II** was carried out in acetic acid with sodium nitrite.[49]

The reaction progress and purity of products was examined by thin layer chromatography (TLC), using silica gel plates Sorbfil PTSKh-AF-V as stationary phase in a ethyl acetate - toluene (1: 5) system, spot visualization in UV light.

*General procedure for the preparation of compounds **IV** and **V**.*

To solution of compound **III** (1 g, 4.15 mmol, 1 eq.) in ethanol (8 ml) at 45^{0}C alkyl hydrazine (5.81 mmol, 1.4 eq) was added slowly dropwisely during 15 min, the reaction mixture was stirred at room temperature for 1 h, and at 0-10 ^{0}C for 4 h. Mixture was allowed to stand at -15 ^{0}C for 24 h, the blue-green precipitate of nitrosopyrazole **V** was filtered off and washed with ice-cold aqueous ethanol (5 ml). Filtrate was added in water (80 ml), the green resin was salted out with sodium chloride and was adsorbed on silica gel. Nitrosopyrazole **IV** was purified by chromatography (silica gel; ethylacetate - heptane, 1:5).

An analytically pure sample of nitrosopyrazole **V** was also obtained using column chromatography under the same conditions.

1,3-dimethyl-5-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (IVa): blue oil, yield 0.037 g (4%);^{1}H NMR (600 MHz, $CDCl_3$):δ = 7.54 - 8.12 (m, 7H; Ar-H), 3.67 (s, 3H; CH_3), 2.45 ppm (brs, 3H; CH_3);^{13}C NMR (150 MHz, $CDCl_3$):δ = 160.61 (C4, Pyr), 133.51, 131.82, 130.84, 129.62, 128.66, 127.45, 126.51, 125.01, 124.57, 124.47, 124.43, 36.83 (1-Pyr-CH_3), 13.10 ppm (3-Pyr-CH_3);IR: ν̃ = 1511 (w), 1334 (vs)см$^{-1}$ (N=O);UV-Vis (ethanol): λ_{max} (ε) =684 (70) (N=O), 294 nm (18230 mol^{-1}dm^{3}cm^{-1});HPLC/MS (6kV): m/z (%): 251 (14) $[M]^+$, 248 (100), 143 (55) $[C_{11}H_{11}]^+$, 127 (41) $[C_{10}H_7]^+$; elemental analysis calcd (%) for $C_{15}H_{13}N_3O$: C 71.70, H 5.21, N 16.72; found: C 71.64, H 5.09, N 16.81.

1,5-dimethyl-3-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (Va): blue green crystals, yield 0.43 g (42%); mp 115 ^{0}C;^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.99 (m, 7H, Ar-H), 3.98 (s, 3H, CH_3), 2.80 (br s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.91 (C4, Pyr), 133.47, 131.75, 129.54, 129.06, 128.25, 126.37, 125.76, 125.33, 124.89, 35.98 (1-Pyr-CH_3), 10.27 (5-Pyr-CH_3); IR: ν̃ = 1500 (w), 1325 (vs) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 685 (57) (N=O), 292 nm (12580 mol^{-1}dm^{3}cm^{-1});MS (70 eV): m/z (%): 251 (1.10) $[M]^+$, 235 (17.42) $[M - O]^+$, 234 (100) $[M- OH]^+$, 153 (7.71) $[C_{11}H_7N]^+$; elemental analysis calcd (%) for $C_{15}H_{13}N_3O$: C 71.70, H 5.21, N 16.72; found: C 71.74, H 5.18, N 16.79.

1-ethyl-3-methyl-5-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (IVb): blue oil, yield 0.15 g (14%);^{1}H NMR (600 MHz, $[D_6]$DMSO): δ = 7.49-8.24 (m, 7H, Ar-H), 3.93 (sext, $^3J_{H,H}$=7.1 Hz, 1H, $\underline{H_A}$-CH_B-CH_3), 3.84 (sext, $^3J_{H,H}$=7.1 Hz, 1H, H_A-$C\underline{H_B}$-CH_3), 2.37 (br s, 3H, CH_3), 1.26 (t, $^3J_{H,H}$=7.2 Hz, 3H, CH_2-CH_3); ^{13}C NMR (150 MHz, $[D_6]$DMSO): δ = 161.37 (C4, Pyr), 133.35, 132.03, 131.00, 129.81, 128.94, 127.95, 127.01, 125.73, 124.80, 124.75, 44.75 (1-Pyr-$\underline{CH_2}$-CH_3), 14.96(1-Pyr-CH_2-$\underline{CH_3}$), 13.42 (3-Pyr-CH_3);IR: ν̃ = 1500 (w), 1332 (vs) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 685 (81) (N=O), 295 nm (18100 mol^{-1}dm^{3}cm^{-1});HPLC/MS (6 kV): m/z (%): 265 (100) $[M]^+$, 264 (50) $[M-H]^+$; elemental analysis calcd (%) for $C_{16}H_{15}N_3O$: C 72.43, H 5.70, N 15.84; found: C 72.56, H 5.56, N 15.74.

1-ethyl-5-methyl-3-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (Vb): blue green crystals, yield 0.51 g (46%); mp 108 ^{0}C;^{1}H NMR (600 MHz, $[D_6]$DMSO): δ = 7.44-8.07 (m, 7H, Ar-H), 4.30 (q, $^3J_{H,H}$=7.2 Hz, 2H, $\underline{CH_2}$-CH_3), 2.84 (br s, 3H, CH_3), 1.47 (t, $^3J_{H,H}$=7.2 Hz, 3H, CH_2-$\underline{CH_3}$); ^{13}C NMR (150 MHz, $[D_6]$DMSO): δ = 160.51 (C4, Pyr), 131.63, 130.41, 129.55, 129.12, 128.60, 126.87, 126.35, 125.44, 44.17 (1-Pyr-$\underline{CH_2}$-CH_3), 14.59 (5-Pyr-CH_3), 10.06 (1-Pyr-CH_2-$\underline{CH_3}$);IR: ν̃ = 1346 (vs), 1500 (w) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 685 (80) (N=O), 295 nm (23100mol^{-1}dm^{3}cm^{-1});MS (70 eV): m/z (%): 265 (1.50) $[M]^+$, 235 (24.35) $[M - O]^+$, 234 (100) $[M - OH]^+$, 179 (7.51) $[C_{12}H_7N_2]^+$, 153 (10.91) $[C_{11}H_7N]^+$, 42 (12.71) $[CNO]^+$; elemental analysis calcd (%) for $C_{16}H_{15}N_3O$: C 72.43, H 5.70, N 15.84; found: C 72.48, H 5.41, N 15.80.

3-methyl-5-(naphthalen-1-yl)-4-nitroso-1-propyl-1H-pyrazole (IVc): blue oil, yield 0.09 g (8%);^{1}H NMR (600 MHz, $[D_6]$DMSO): δ = 7.49-8.12 (m, 7H, Ar-H), 3.95 (p, $^3J_{H,H}$=6.8 Hz, 1H, H_A-$C\underline{H_B}$-CH_2-CH_3), 3.73 (p, $^3J_{H,H}$ = 7.0 Hz, 1H, $\underline{H_A}$-CH_B-CH_2-CH_3), 2.36 (br s, 3H, CH_3), 1.70 (m, $J_{H,H}$=7.1 Hz, 2H, CH_2-$\underline{CH_2}$-CH_3), 0.67 (t, $^3J_{H,H}$=7.4 Hz, 3H, CH_2-CH_2-$\underline{CH_3}$); ^{13}C NMR (150 MHz, $[D_6]$DMSO): δ = 161.28 (C4, Pyr), 133.35, 132.06, 131.00, 129.94, 128.93, 127.91, 126.98, 125.68, 124.83, 124.77, 51.06 (1-Pyr-$\underline{CH_2}$-CH_2-CH_3), 22.34 (1-Pyr-CH_2-$\underline{CH_2}$-CH_3), 13.38 (3-Pyr-CH_3), 11.05 (1-

Pyr-CH_2-CH_2-$\underline{CH_3}$); IR: ν˜ = 1511 (w), 1334 (vs), см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 681 (48) (N=O), 293 nm (19300mol^{-1}dm^{3}cm^{-1});HPLC/MS(6kV): m/z (%): 279 (9) $[M]^+$, 278 (43) $[M-H]^+$, 143 (100) $[C_{11}H_{11}]^+$, 127 (16) $[C_{10}H_7]^+$; elemental analysis calcd (%) for $C_{17}H_{17}N_3O$: C 73.10, H 6.13, N 15.04; found: C 73.22, H 6.08, N 14.97.

5-methyl-3-(naphthalen-1-yl)-4-nitroso-1-propyl-1H-pyrazole (Vc): blue green crystals, yield 0.6 g (53%); mp 106 ^{0}C;^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 7.44-8.08 (m, 7H, Ar-H), 4.24 (t, $^3J_{H,H}$=7.1 Hz, 2H, $\underline{CH_2}$-CH_2-CH_3), 2.84 (br s, 3H, CH_3), 1.92 (sext, $^3J_{H,H}$=7.3 Hz, 2H, CH_2-$\underline{CH_2}$-CH_3), 0.97 (t, $^3J_{H,H}$=7.4 Hz, 3H, CH_2-CH_2-$\underline{CH_3}$); ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 160.46 (C4, Pyr), 133.30, 131.65, 129.56, 129.09, 128.62, 126.89, 126.35, 125.44, 125.41, 50.40 (1-Pyr-$\underline{CH_2}$-CH_2-CH_3), 22.50 (5-Pyr-CH3), 11.19 (1-Pyr-CH_2-$\underline{CH_2}$-CH_3), 10.21 (1-Pyr-CH_2-CH_2-$\underline{CH_3}$);IR: ν˜ = 1344 (vs), 1500 (w) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 680 (51) (N=O), 293 nm (12800mol^{-1}dm^{3}cm^{-1});MS (70 eV): m/z (%): 279 (1.40) $[M]^+$, 263 (23.72) $[M-O]^+$, 262 (100) $[M-OH]^+$, 179 (11.61) $[C_{12}H_7N_2]^+$, 153 (7.61) $[C_{11}H_7N]^+$, 42 (9.81) $[CNO]^+$; elemental analysis calcd (%) for $C_{17}H_{17}N_3O$: C 73.10, H 6.13, N 15.04; found: C 73.17, H 6.11, N 15.10.

1-isopropyl-3-methyl-5-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (IVd): blue solid, yield 0.26 g (22%); mp 116 ^{0}C;^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50-8.11 (m, 7H, Ar-H), 4.21 (septet, $^3J_{H,H}$= 6.6 Hz, 1H, CH), 2.48 (br s, 3H, CH_3), 1.47 (d, $^3J_{H,H}$= 6.7 Hz, 3H, CH-(CH_3)CH_3'), 1.45 (d, $^3J_{H,H}$= 6.7 Hz, 3H, (CH_3)CH_3'); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 160.74 (C4, Pyr), 133.47, 132.33, 130.52, 130.32, 129.02, 128.51, 127.50, 127.21, 126.50, 125.01, 124.64, 124.05, 50.98 (1-Pyr-$\underline{CH}$-(CH_3)CH_3), 22.49 (1-Pyr-CH-(CH_3)$\underline{CH_3}$), 21.53 (1-Pyr-CH-($\underline{CH_3}$)CH_3), 13.35 (3-Pyr-CH_3);IR: ν˜ = 1332 (vs), 1536 (w) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε) = 682 (45) (N=O), 296 nm (12300mol^{-1}dm^{3}cm^{-1});MS (70 eV): m/z (%): 279 (31.93) $[M]^+$, 263 (23.52) $[M-O]^+$, 262 (100) $[M-OH]^+$, 179 (10.61) $[C_{12}H_7N_2]^+$; elemental analysis calcd (%) for $C_{17}H_{17}N_3O$: C 73.10, H 6.13, N 15.04; found: C 72.96, H 6.21, N 15.34.

1-isopropyl-5-methyl-3-(naphthalen-1-yl)-4-nitroso-1H-pyrazole (Vd): blue green crystals, yield 0.53 g (46%); mp 130 ^{0}C;^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43-7.98 (m, 7H, Ar-H), 4.67 (septet, $^3J_{H,H}$= 6.7 Hz, 1H, CH), 2.81 (br s, 3H, CH_3), 1.66 (d, $^3J_{H,H}$= 6.7 Hz, 6H, CH-($\underline{CH_3}$)$_2$); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.96 (C4, Pyr), 133.55, 131.78, 129.43, 129.22, 128.61, 128.23, 126.28, 125.70, 125.45, 124.92, 50.22 ($\underline{CH}$-(CH_3)$_2$), 21.82 (CH-($\underline{CH_3}$)$_2$), 9.90 (5-Pyr-CH_3); IR: ν˜ = 1330 (vs), 1532 (w) см$^{-1}$ (N=O); UV-Vis (ethanol): λ_{max} (ε)= 682 (84) (N=O), 294 nm (16700mol^{-1}dm^{3}cm^{-1});MS (70 eV): m/z (%): 279 (2.3) $[M]^+$, 263 (20.22) $[M-O]^+$, 262 (100) $[M-OH]^+$, 179 (21.13) $[C_{12}H_7N_2]^+$, 153 (9.11) $[C_{11}H_7N]^+$; elemental analysis calcd (%) for $C_{17}H_{17}N_3O$: C 73.10, H 6.13, N 15.04; found: C 73.15, H 6.09, N 15.12.

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Keywords:nitrogen heterocycles•nitrosopyrazole •NMR spectroscopy•quantum chemical calculations•X-ray powder diffraction analysis

[1] M. Konwar, P. Phukan, Dr. A. K. Chaliha, Prof. A. K. Buragohain, K. Damarla, D. Gogoi, Dr. A. Kumar, Dr. D. Sarma.*ChemistrySelect,***2019**, 35, 10236–10245.
[2] H. M. F. Elnagdy, Dr. D. Sarma. *ChemistrySelect,***2019**, 3, 783–787.
[3] R. P. Bhaskaran, Dr. J. C. Janardhanan, Dr. B. P. Babu. *ChemistrySelect,***2020**, 16, 4822–4825.
[4] Dr. M. Gümüş, N. Gümüş, Prof. H. E. Eroğlu, Prof. İ. Koca. *ChemistrySelect***2020,** 20, 5916–5921.
[5] C. Alka, P.K. Sharma, K. Niranjan.*Int. J. Chem. Tech. Res.***2011**, 1, 11-15.
[6] R. E. Orth.*Pharm. Sci.***1968**, 57, 4, 537-556.
[7] E. Tzanetou, S. Liekens, K.M. Kasiotis. *Arch. Pharm. Chem. Life Sci.***2012**, 345, 10, 804-820.
[8] Z. Tabarelli, M.A. Rubin, D.B. Berlese, P.D. *J. Med. Biol. Res.***2004**, 37, 1531- 1540.
[9] V. Kumar, K. Kaur, G. K. Gupta, A. K. Sharma. *Eur. J. Med. Chem.***2013**, 69, 735–753.
[10] J.-W.Yuan, S.-F.Wang, Z.-L.Luo, H.-Y.Qiu, P.-F.Wang, X.Zhang, H.-L.Zhu.*Bioorg. Med. Chem. Lett.***2014**,24, 2324–2328
[11] J. L.Díaz, R.. Cuberes, J. Berrocal, M. Contijoch, U. Christmann, A. Fernández, C.Almansa.*J. Med. Chem*. **2012**, 55, 8211–8224.
[12] P. J. Jainey, B. K. Ishwar, J. Neethu. *Asian J. Pharm. Clin. Res.***2017**, 10, 4, 456-459.
[13] Avinash C. Tripathi, Savita Upadhyay, Sarvesh Paliwal, Shailendra K. Saraf. *EXCLI Journal*.**2018**, 17, 126-148.
[14] A. S. Abu-Surrah, K. A. Abu Safieh, I. M. Ahmad, M. Y. Abdalla, M. T. Ayoub, A. K. Qaroush, A. M. Abu-Mahtheieh. *Eur. J. Med. Chem*. **2010**, 45, 471–475.
[15] S. Y. Shin, Y. Lee, J. Park, D. Hwang, G. Jo, J. H. Lee, Y. Lim. *Appl. Biol. Chem.*. **2018**, 61, 6, 697–701.
[16] B. S. Kim, S. Y. Shin, S. Ahn, D. Koh, Y. H. Lee, & Y. Lim. *Bioorg. Med. Chem.***2017**, 25, 5423–5432.
[17] P. Horrocks, M. R. Pickard, H. H. Parekh, S. P. Patel, R. B. Pathak. *Organic & Biomolecular Chemistry*.**2013**, 11, 29, 4891-4898.
[18] R. C. Khunt, V. M. Khedkar, R. S. Chawda, N. A. Chauhan, A. R. Parikh & E. C. Coutinho. *Bioorg. Med. Chem. Lett.***2012**, 22, 1, 666–678.
[19] O. G. Khudina, Ya. V. Burgart,a V. I. Saloutin, M. A. Kravchenko. *Russ. Chem. Bull*.**2010**, 59, 10, 1967—1973.
[20] M. Ahn, P. Gunasekaran, G. Rajasekaran, E.Y. Kim, S.-J.Lee, G. Bang, K. Cho, J.-K.Hyun, H.-J.Lee, Y.H. Jeon, N.-H. Kim, E.K. Ryu, S.Y. Shin, J.K. Bang. *Eur. J. Med. Chem.* **2016**, 125, 551-554
[21] J. B. Shi, W. J. Tang, B. qi Xing, R..Li & X. H. Liu.*Eur. J. Med. Chem.* **2015**, 90, 889–896.
[22] X.-F. Huang, X. Lu, Y. Zhang, G.-Q.Song, Q.-L.He, Q.-S.Li, H.-L.Zhu.*Bioorg. Med. Chem.***2012**, 20, 16, 4895–4900.
[23] M. Comes Franchini, B. F. Bonini, C. M. Camaggi, D. Gentili, A. Pession, M. Rani, & E. Strocchi. *Eur. J. Med. Chem.***2010**, 45, 5, 2024–2033.
[24] N. R. Emmadi, C. Bingi, S. S. Kotapalli, R. Ummanni, J. B. Nanubolu, & K. Atmakur.*Bioorg. Med. Chem. Lett.***2015**, 25, 2918–2922.
[25] a) M. Cameron, B. G. Gowenlock, A. S. F. Boyd. *J. Chem. Soc., Perkin Trans. 2.***1996**, 2271-2274.b)D. A. Fletcher, B. G. Gowenlock,K. G. Orrell, V. Sik, D. E. Hibbs, M. B. Hursthouse, K. M. Abdul Malik. *J. Chem. Soc., Perkin Trans. 2.***1997**, 721-728.
[26] V. V. Efimov, E. V. Neupokoeva, I. V. Peterson, A. V. Lyubyashkin, G. A. Suboch, M. S. Tovbis.*Russ. J. Org. Chem.*. **2019**,55,8,1081-1084.
[27] A.D. Becke. *Phys. Rev. A.* 1988, 38, 3098-3100.
[28] C. Lee, W. Yang, R.G. Parr. *Phys. Rev. B.* 1988, 37, 785-789.
[29] S. Grimme, S. Ehrlich, L. Goerigk. *J. Comput. Chem*. **2011**, 32, 1456-1465.
[30] S. Grimme, J. Antony, S. Ehrlich, H. Krieg. *J. Chem. Phys.***2010**, 132, 154104.
[31] R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople. *J. Chem. Phys*. **1980**,72, 650-654.
[32] F. Neese. *WIREs Comput. Mol. Sci*. **2012**, 2, 73-78.
[33] F. Neese. *WIREs Comput*. *Mol.Sci*. **2017**, 8, e1327.
[34] W. Yang, W.J. Mortier. *J. Am. Chem. Soc*.**1986**, 108, 5708-5711.

[35] A.E. Reed, R.B. Weinstock, F. Weinhold.*J. Chem. Phys*. **1985**, 83, 735-746.
[36] T.Y. Nikolaienko, L.A. Bulavin, D.M. Hovorun. *Comput. Theor. Chem.***2014**, 1050, 15-22
[37] T.Y. Nikolaienko, L.A. Bulavin. *Int. J. Quantum Chem*. **2019**, 119, e25798
[38] F.H. Allen.*Acta Crystallogr.***2002**, 380–388.
[39] S.D. Kirik, S.A. Kovyazin, A.M. Fedotov. *Powder Diffraction.* **1990**, 5, 4, 181-185
[40] a) Yu. A. Alemasov, D. G. Slaschinin, M. S. Tovbis, S.D. Kirik.*J. Mol. Struct.***2010**, 985, 184-190. b) D. G. Slaschinin, Y. A. Alemasov, D. I. Ilushkin, W. A. Sokolenko, M. S. Tovbis, S.D. Kirik.*J. Mol. Struct.***2012**, 1015, 173-180. c) D.Y. Leshok,N.A.Fedorova, D.G. Slaschinin,M.S. Tovbis, S.D. Kirik. *J. Mol. Struct.***2014**, 1063, 341-350.
[41] J. W. Visser.*J. Appl. Crystallogr*. **1969**, 2, 89−95.
[42] S. D.Kirik, S. V.Borisov, V. E. Fedorov.*Zh. Strukt. Khim*. **1981**, 22, 131−135.
[43] A. Le Bail, Y. Gao, J. L. Fourquet, C. Jacoboni.*Mater.Res.Bull.***1990**, 25, 831−839.
[44] L. A. Solovyov, S. D. Kirik. *Mater. Sci. Forum*.**1993**, 195−200.
[45] V. Favre-Nicolin, R. Cerný. *J.Appl.Crystallogr.***2002**, 35, 734−743.
[46] S.D. Kirik.*Crystallography.***1985**, 30, 185−187.
[47] J. Rodriguez-Carvajal. FullProf, version 4.06, March 2009. ILL, unpublished. can be found under https://www.psi.ch/sites/default/files/import/sinq/dmc/ManualsEN/fullprof.pdf
[48] A. Banchetti. *Gazz. Chim. Ital*. **1940**, 70, 134-144.
[49] L. Wolff. *Justus Liebigs Ann. Chem.***1902**, 325, 136

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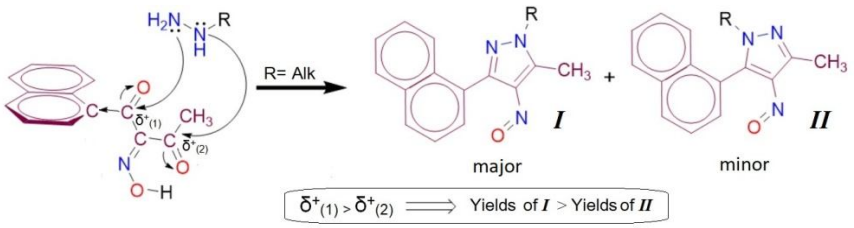

In the initial 2-(hydroxyimino)-1-(naphthalen-1-yl)butane-1,3-dione the electrophilicity of the “naphthalene” carbonyl group is higher than that of the second carbonyl group. For this reason, the formation of nitrosopyrazole **I** dominates compared to **II**.