QUANTUM-CHEMICAL STUDY OF THE STRUCTURE AND THERMOCHEMICAL PROPERTIES OF NITROPIPERAZINES AND NITROSOPIPERAZINES

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We have used MNDO and PM3 approximations and the density functional method (6-31G*) for a quantum chemical study of the structure and some physicochemical properties of N-nitro and N-nitroso derivatives of piperazine, furazano[3,4-b]piperazine, and bisfurazano[3,4-b;3',4'-e]piperazine. We have analyzed the structural, electronic, and thermochemical characteristics and the enthalpies of formation for the compounds in the gas phase and in the solid phase. We have found a correlation between the strength of the N–N bond and the N–N bond length, the pyramidality of the nitrogen atom of the piperazine ring, and the size of the energy gap between the frontier orbitals. Based on calculations by the density functional method, we have carried out a comparative analysis of the thermochemical stability of the compounds in homolytic reactions.

Nitramines (N-nitro compounds) occupy a central position among components of high energy compositions [1-5]. In the field of design of high energy substances as a whole and nitramines in particular, considerable attention has been paid to developing methods for theoretical analysis of their structure and prediction of the properties of these compounds before the synthesis stage [2, 4, 6, 7].

The piperazine ring is rather widely used as the base structure in designing high energy substances. Thus N-nitropiperazines and N-nitrosopiperazines and their polynitrogen annelated derivatives have been suggested as components of explosive compositions, propellants, and rocket fuels [8-12]. The compounds in this group in future may be considered as components of gas-generating compositions.

The "parent" compound of this series, N,N'-dinitropiperazine, is a quite thermally stable compound with decomposition temperature 190-200°C [5]. The stability of its analogs containing substituents or annelated heterocycles on the carbon atoms is different, and is determined by the nature of their structural differences. Some known nitropiperazines and their decomposition temperatures are given below:


190-200°C [5]   302°C [10]   236°C [13]   238°C [10]

220°C [10]   210°C [10]   134°C [12]

206°C [8]   148°C [9]   99°C [9]
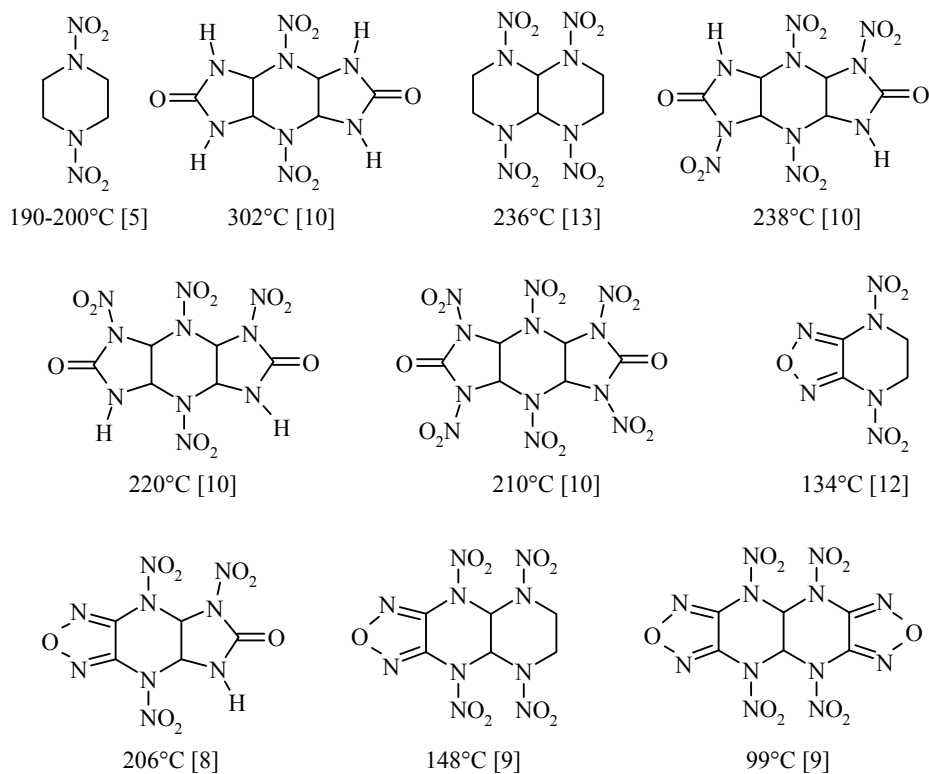
Thermal decomposition of most secondary N-nitramines begins with homolytic breaking of the $N-NO_2$ bond [14, 15]. It is hypothesized that decomposition also begins with homolytic breaking of the N–N bond in N-nitroso compounds [16]. In this case, if the nitrogen atom bonded to the nitro group is involved in conjugation processes or nonvalence orbital interactions with the functional group on the adjacent carbon atom, the strength of the N–N bond is observed to decrease, which facilitates either breaking of the bond according to a radical mechanism or a 1,3-sigmatropic shift of the nitro group. As a result, the thermal stability of such compounds decreases [17]. Piperazine derivatives are no exception in this sense, and so analysis of the relations between structural variations and properties of derivatives of nitrosopiperazine and nitropiperazine is certainly of interest. In extending our studies of high energy derivatives of furazan [18-20], for which high thermal stability is typical [15, 21], it seemed of interest to estimate the characteristics of nitro and nitroso derivatives and some other polycyclic compounds that include both furazan and piperazine rings. Various aspects of the chemistry of furazanopiperazines have been discussed in a recent review [22].

The aim of this work was to study the geometric and electronic structure and enthalpies of formation for nitro and nitroso derivatives of piperazine **1**, furazano[3,4-*b*]piperazine **2**, bisfurazano[3,4-*b*;3',4'-*e*]piperazine **3**, 5,6-dioxofurazano[3,4-*b*]piperazine **4**, and 5,6-dihydroximinofurazano[3,4-*b*]piperazine **5**. Estimation of the relative strength of the N–N bonds and also the enthalpies of reaction for homolytic decomposition of compounds in these series was an integral part of the investigation:

1   **2**   **3**   **4**   **5**

1569
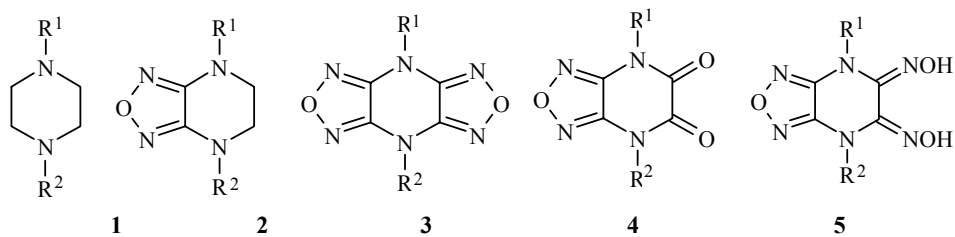
For the calculations, we used the MOPAC [23] and WINMOPAC [24] software packages. The geometric parameters, like the charge distributions, were estimated using the MNDO method [23] as the most applicable in calculations of these characteristics for N,O-containing molecules. The dipole moments, ionization potentials, and energies of frontier molecular orbitals were calculated by the MNDO and PM3 methods [23]; the enthalpies of formation for the compounds in the gas phase were estimated based on the PM3 method, and in the solid phase they were estimated using additive schemes [25-27]. In cases when the existence of several conformers is possible for the molecule, we estimated the characteristics of only the most thermodynamically stable characteristics.

CALCULATION OF GEOMETRIC PARAMETERS OF THE MOLECULES

According to the results of our study estimating the geometric characteristics of the compounds (Tables 1 and 2), both for the nitro and the nitroso derivatives, as we go from the monofurazanoannelated and then to the difurazanoannelated compounds the N–N bond length increases, which suggests the bond is weakened in this order. Thus in the nitroso compounds **1b,d,e**, the bond length is 1.34 Å, increasing up to 1.36 Å in compounds **2b,d,e** and up to 1.38 Å in the corresponding derivatives of series **3** and **4**. Analogous changes were detected by X-ray diffraction; thus the N–N bond length in N,N'-dinitropiperazine (**1d**) [28] is equal to 1.34 Å, while in N,N'-dinitrosofurazano[3,4-*b*]piperazine (**2d**) [29] the bond length increases up to 1.36 Å. In nitro derivatives **1**, according to the calculations, the N–NO_2 bond is equal to 1.40 Å (**1c**), 1.42 Å (**1e**), and 1.41-1.42 Å (**1f**), increasing in the corresponding monofurazanoannelated and then the difurazanoannelated derivatives up to 1.44 Å (**2c**), 1.43 Å (**2e**), and 1.44 Å (**2f**). The calculations are supported by the results of the X-ray diffraction studies: thus , the N–NO_2 bond has a length of 1.37 Å* in N,N'-dinitropiperazine (**1f**), while in N,N'-dinitrofurazano[3,4-*b*]piperazine (**2f**) the bond length is 1.38 Å [30].

The calculations presented in Table 1 allow us to conclude that for both nitro and nitroso derivatives, adding any functional group to the carbon atom of the piperazine ring that involves the nitrogen atom of this ring in conjugation processes or nonvalence orbital interactions is accompanied by lengthening of the N–N bond and a decrease in the bond strength. Substitution of each CH_2–CH_2 moiety of the piperazine ring by a furazan ring also leads to lengthening of the N–N bond by 0.02 Å on the average for nitroso derivatives and by 0.04-0.06 Å for nitro derivatives. The data obtained and the trends found are consistent with the results of experimental investigations (**1d** [28], **1f***, **2d** [29], **2f** [30], **3a** [31]). Comparison of the quantum-chemical calculations for the geometric parameters of the molecules in the gas phase with the X-ray diffraction results for the crystals indicates lengthening (by 1.3-3.6%) of the N–N bonds in the gas phase compared with the solid phase.

Let us also consider such a characteristic of the spatial structure of the compounds as the pyramidality (Δ) (i.e., the difference between 360° and the sum of the bond angles at the N atom) of the nitrogen atom of the piperazine ring. We know that in piperazine and its N-alkyl derivatives, the nitrogen atom has a pyramidal configuration [32]. In contrast, nitrosopiperazines (Table 1) are practically planar (0-0.9°). For nitropiperazines, the pyramidality of the ring nitrogen atom is rather distinctive and depends on the structural variations of the base molecule. Thus the angle of deviation of the N–NO_2 bond of the nitro group from the C–N–C plane of the piperazine ring, which also characterizes the pyramidality of the nitrogen atom, covers the interval from 1.7° (**4e**) to 18.5° (**5e**).

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* Here and in the following, for compound **1f** the data from R. Gillardi (private communication) are marked with an asterisk.

TABLE 1. Calculated (MNDO method) Characteristics of the Spatial Structure and Indices of the Change in Strength [36, 37] of the N–N Bond in Compounds **1-5***

Compound*2	l_{N-N}, Å	i_{N-N}, %	Δ, deg.
1a	—	—	26.63/27.24
1b	1.34	7.2	25.02/0.85
1c	1.40	0	24.64/10.36
1d	1.34	18.3/18.2	0.23/0.36
1e	1.34/1.42	17.5/ 6.3	0.15/11.87
1f	1.42/1.41	9.7/7.9	6.58/10.73
2a	—	—	18.50/18.54
2b	1.36	4.9	18.91/0.41
2c	1.44	0.1	17.55/8.10
2d	1.36	4.2/4.3	0.44/0.49
2e	1.37/1.43	3.4/11.5	0.34/10.18
2f	1.44	-2.5/-0.1	7.94/10.21
3a	—	—	16.77/17.32
3b	1.38	-5.9	16.90/0.02
3c	1.46	-18.1	14.18/15.03
3d	1.38	-6.7/-6.8	0/0.01
3e	1.38/1.46	-7.4/-15.1	0.08/4.94
3f	1.46	-18.6/-18.1	14.26/15.38
4a	—	—	-0.01/0
4b	1.38	-3.3	0.01/0
4c	1.44	-5.7	0.06/1.80
4d	1.38	-5.0/-4.1	0/0.02
4e	1.38/1.44	-4.9/-6.9	0.04/1.70
4f	1.44	-3.4/-2.9	2.77/4.33
5a	—	—	0.11/0.17
5b	1.37	-1.8	0.45/0
5c	1.44	-11.5	15.73/15.73
5d	1.37	-3.3/-3.2	0.63/0.86
5e	1.38/1.44	-3.0/-16.2	0.01/18.50
5f	1.45	-9.0/-9.6	15.02/15.03

* l_{N-N} is the N–N bond length; i_{N-N} is the index of the change in strength of the N–N bond; Δ is the pyramidality of the nitrogen atoms (i.e., the difference between 360°C and the sum of the angles at the N atom of the piperazine ring).

*2 **1-5 a-c** R^1 = H, **d,e** R^1 = NO, **f** R^1= NO$_2$; **a** R^2 = H, **b,d** R^2 = NO, **c,e,f** R^2 = NO$_2$.

Upon condensation of the furazan ring with a piperazine ring, the pyramidality of the nitrogen atoms bonded to the nitro group increases (compounds **4** are an exception) and this is accompanied by lengthening of the N–NO$_2$ bond. The strength of the N–N bond consequently decreases, which is consistent with experimental data on the thermal stability of secondary nitramines [33-35].

Let us consider the conformations of the piperazine ring of the studied series of compounds, taking the dinitro derivatives as an example. The results of calculations of the geometry for molecules **1** suggest that the piperazine ring in those molecules has a *chair* conformation (Fig. 1). This is consistent with X-ray diffraction data for N,N'-dinitrosopiperazine (**1d**) [28] and N,N'-dinitropiperazine (**1f**).

TABLE 2. Calculated Characteristics of the Electronic Structure and Enthalpies of Formation for Compounds **1-5** in the Gas and Solid Phases*

Com-pound	μ, D		Ionization potential, eV		Δ, eV		ΔH_f^0, kcak/mol	
	MNDO	PM3	MNDO	PM3	MNDO	PM3	PM3 (MOPAC) (gas phasea)	Additive scheme (solid phase)
1	3	4	5	6	7	8	9	10
1a	2.02	2.04	9.908	9.224	-9.908/2.873 (12.781)	-9.224/2.562 (11.786)	-11.7	-10.9 (-10.9)*[2]
1b	2.40	2.56	10.048	9.629	-10.048/0.512 (10.560)	-9.629/0.313 (9.942)	22.0	5.0
1c	3.97	3.24	10.585	9.854	-10.585/-0.233 (10.352)	-9.854/-0.012 (9.842)	5.8	-7.0
1d	0.02	0.00	10.417	9.956	-10.417/0.278 (10.695)	-9.956/0.042 (9.914)	26.6	22.2
1e	1.73	1.52	10.876	10.210	-10.876/-0.535 (10.341)	-10.210/-0.222 (9.988)	-3.9	8.0
1f	1.59	1.54	11.408	10.912	-11.408/-0.715 (10.693)	-10.912/-0.378 (10.534)	-33.5	-13.2 (-12.7)*[3]
2a	5.01	5.19	9.819	9.502	-9.819/-0.259 (9.560)	-9.502/-0.510 (8.992)	55.0	38.0
2b	4.98	5.01	10.099	9.898	-10.099/-0.685 (9.414)	-9.898/-0.868 (8.982)	82.1	70.0
2c	5.65	5.18	10.570	10.087	-10.570/-1.223 (9.347)	-10.087/-1.082 (9.005)	52.3	59.0

TABLE 2 (continued)

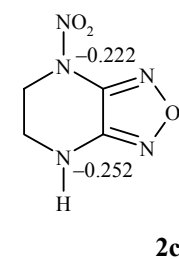| 1	3	4	5	6	7	8	9	10
2d	3.92	3.59	10.371	10.307	-10.307/-0.949 (9.422)	-10.307/-1.225 (9.082)	110.7	105.0
2e	7.15	6.50	10.423	10.030	-10.423/-1.205 (9.218)	-10.030/-1.206 (8.824)	79.3	91.0
2f	4.24	4.00	11.286	10.799	-11.286/-1.675 (9.611)	-10.799/-1.479 (9.320)	84.0	84.0
3a	1.79	0.99	10.184	9.801	-10.184/-1.261 (8.923)	-9.801/-1.528 (8.273)	130.5	93.4
3b	1.41	1.53	10.335	10.063	-10.335/-1.370 (8.965)	-10.063/-1.640 (8.423)	162.1	135.0
3c	2.99	1.52	10.794	10.128	-10.794/-1.987 (8.807)	-10.128/-1.849 (8.279)	130.3	124.0
3d	0.07	0.06	9.919	9.718	-9.919/-1.042 (8.877)	-9.718/-1.350 (8.368)	194.3	187.0
3e	1.97	0.29	10.933	10.391	-10.933/-2.090 (8.843)	-10.391/-1.988 (8.403)	168.0	173.0
3f	0.39	0.39	11.396	10.490	-11.396/-2.366 (9.030)	-10.490/-1.997 (8.493)	141.3	184.9
4a	0.07	0.41	10.402	10.130	-10.402/-1.305 (9.097)	-10.130/-1.564 (8.566)	-27.2	-51.3
4b	1.43	1.33	10.707	10.423	-10.707/-1.458 (9.249)	-10.423/-1.640 (8.783)	5.8	-35.2
4c	2.92	1.16	10.976	10.428	-10.976/-1.768 (9.208)	-10.428/-1.829 (8.599)	28.9	-21.1
4d	0.35	0.09	11.016	10.815	-11.016/-1.563 (9.453)	-10.815/-1.628 (9.187)	39.3	-19.0

TABLE 2 (continued)

1	3	4	5	6	7	8	9	10
4e	1.76	0.28	11.315	10.851	-11.315/-1.945 (9.370)	-10.851/-1.956 (8.895)	8.2	-34.7
4f	0.28	0.17	11.618	10.886	-11.618/-2.374 (9.244)	-10.886/-2.097 (8.807)	-21.6	-50.4
5a	4.27	3.79	9.771	9.554	-9.771/-0.783 (8.988)	-9.554/-1.118 (8.436)	70.5	82.2
5b	4.99	4.60	10.052	9.831	-10.052/-0.861 (9.191)	-9.831/-1.168 (8.665)	100.2	98.3
5c	5.47	4.33	10.278	9.839	-10.278/-1.449 (8.829)	-9.839/-1.422 (8.417)	70.6	82.6
5d	4.95	4.52	10.374	10.264	-10.374/-1.028 (9.346)	-10.274/-1.259 (9.015)	131.4	114.5
5e	4.79	4.25	10.661	10.362	-10.661/-1.554 (9.107)	-10.362/-1.572 (8.790)	101.3	98.8
5f	4.06	3.92	11.143	10.460	-11.143/-1.801 (9.342)	-10.460/-1.646 (8.814)	76.5	83.1

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* μ is the dipole moment; Δ is the HOMO/LUMO energies; ΔH_f^0 is the enthalpy of formation; the charges on the atoms (MINDO) are given on pp. 1572, 1573.
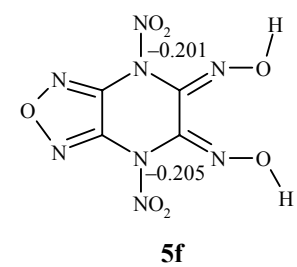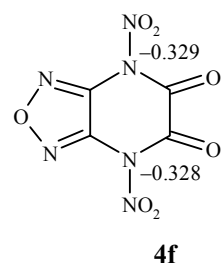
*2 In parentheses we give the experimental value of ΔH_f^0 in the solid phase [26, 40].

*3 The value of ΔH_f^0 in the solid phase [41].

Charges on the Atoms in Compounds **1-5**

1a

2a

3a

4a

5a

1b

2b

3b

4b

5b

1c

2c

3c

4c

5c

1d

2d −0.331 −0.331
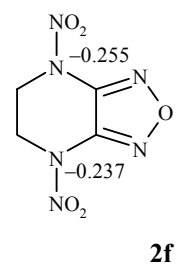
3d −0.245 −0.245

4d −0.342 −0.346

5d −0.290 −0.291

−0.409 −0.409

1e −0.416 −0.340

2e −0.334 −0.243

3e −0.115 −0.247

4e −0.343 −0.331

5e −0.290 −0.207

1f −0.353 −0.357

2f −0.255 −0.237

3f −0.132 −0.129

4f −0.329 −0.328

5f −0.201 −0.205
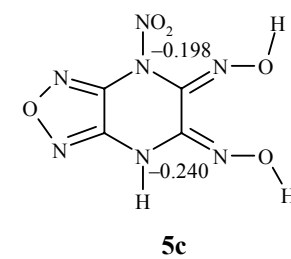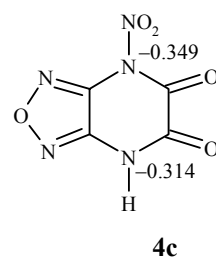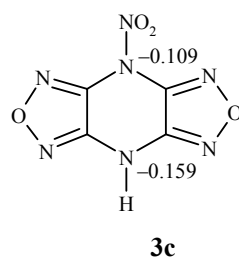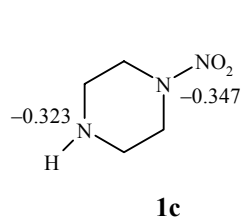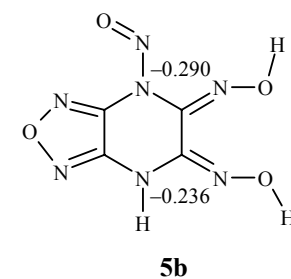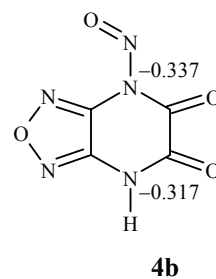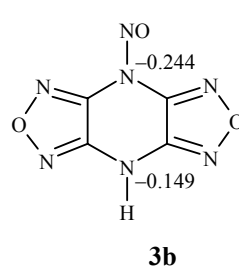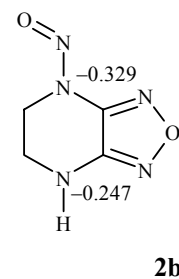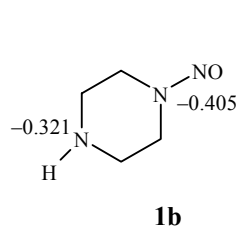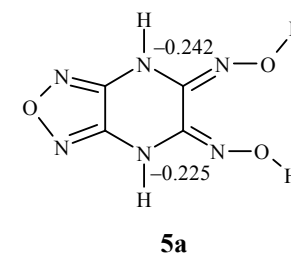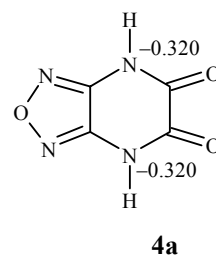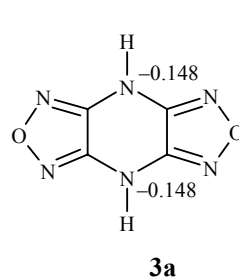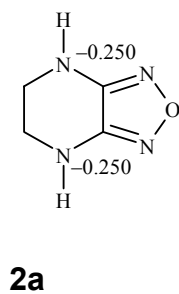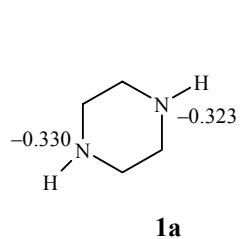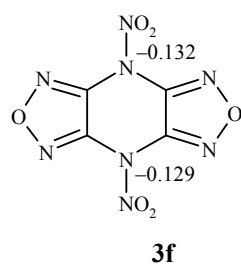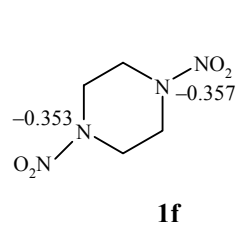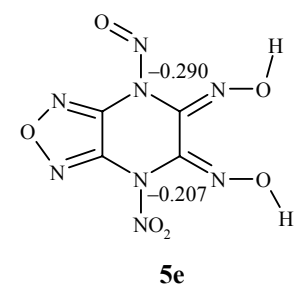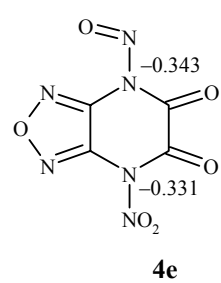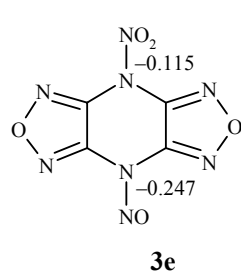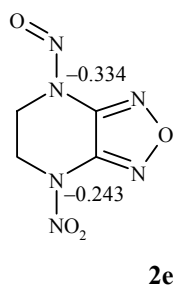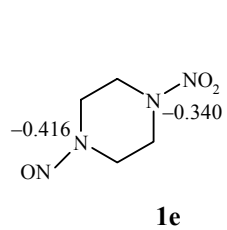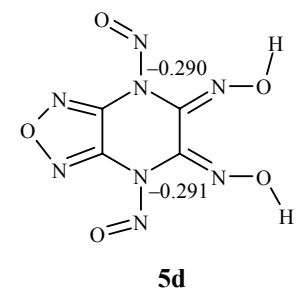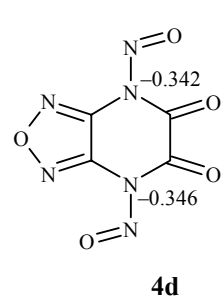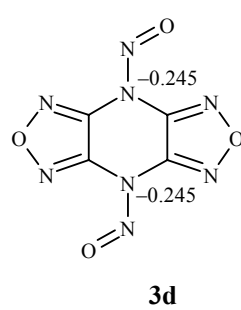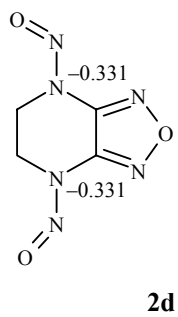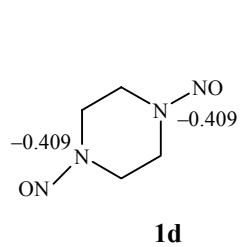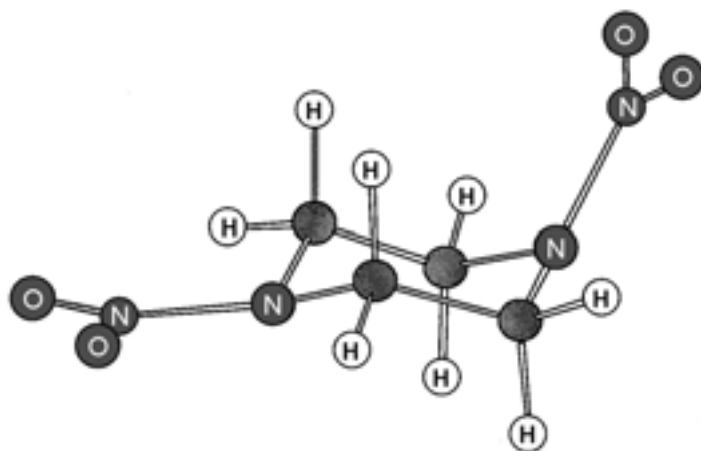
Fig. 1. Spatial structure of the N,N'-dinitropiperazine molecule **1f**.

For compounds **2d,f**, we observe flattening of the piperazine ring and its transition to a *half-chair* conformation **2d** and **2f** (Fig. 2). The X-ray diffraction results for compounds **2d** [29] and **2f** [30] also indicate that in the crystalline state, the piperazine ring has a *half-chair* form in these compounds.

When a second furazan ring is introduced into compounds of series **3**, the piperazine ring has a *boat* conformation (**3a,c,f**) or a *half-chair* conformation (**3b,e**) (Fig. 3). We note that for the compounds in this series, X-ray diffraction data are known only for bisfurazano[3,4-*b*;3',4'-*e*]piperazine (**3a**) [31]; in the crystalline state, the entire tricyclic system is planar. Our calculations of the geometry of the **3d** molecule indicate that in this compound, the tricyclic system is planar (Fig. 3*b*).
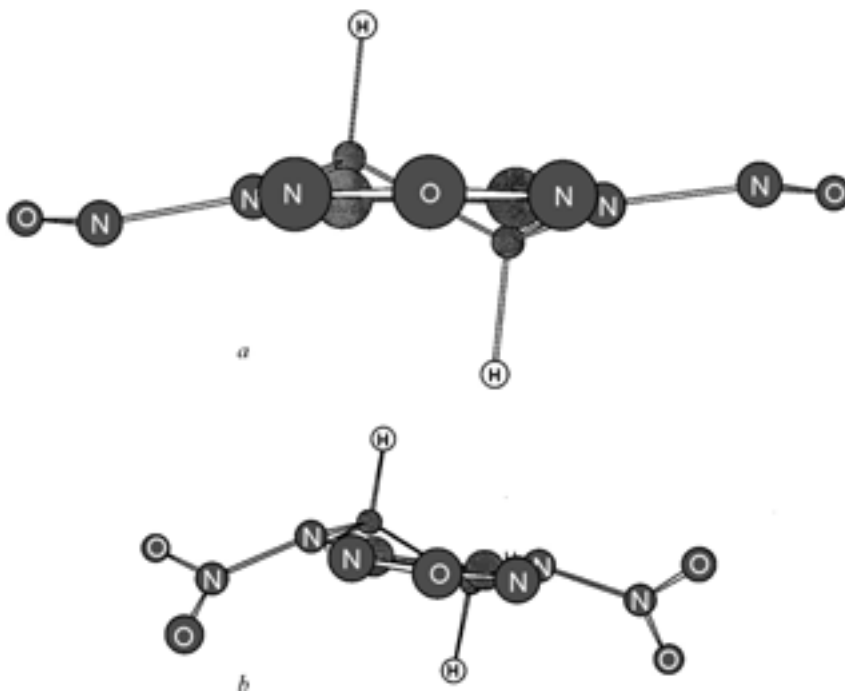
Fig. 2. Spatial structure of the molecules: *a*) N,N'-dinitrosofurazano[3,4-*b*]piperazine **2d**;
b) N,N'-dinitrofurazano[3,4-*b*]piperazine **2f**.
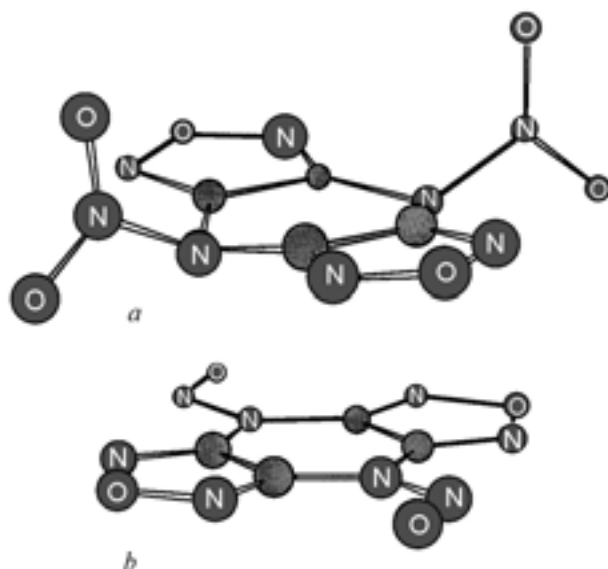
Fig. 3. Spatial structure of the molecules: *a*) N,N'-dinitrobisfurazano[3,4-*b*;3',4'-*e*]piperazine **3f**;
b) N,N'-dinitrosobisfurazano[3,4-*b*;3',4'-*e*]piperazine **3d**.

In the compounds of series **4a,b**, the furazan and piperazine rings and also both carbonyl oxygen atoms are located in one plane. The presence of nitro and nitroso groups in the molecules **4c-f** (Fig. 4) leads to a slight distortion of the *twist* conformation of the piperazine moiety. In this case, the dihedral angles O=C–C=O successively increase in the following order: **4c** (4.8°) < **4d** (5.1°) < **4e** (15.2°) < **4f** (23.6°).

Substitution of the carbonyl oxygen atoms (series **4**) by hydroximine groups (series **5**) leads to significant distortion of the molecular geometry. Thus in series **5**, only structure **5a**, which does not contain substituents on both nitrogen atoms of the piperazine ring, proved to be planar. All the nitro and nitroso derivatives of this series have a *twist* conformation for the piperazine ring. The hydroximine groups are *skewed* relative to each other by 9.5° (**5b**), 41.5° (**5c**), 57.4° (**5d**), 33.0° (**5e**), 60.1° (**5f**, Fig. 5).

The O–N–N bond angle of the nitroso group in the studied nitroso derivatives is within the range 117.9-119.0°. The O–N–O bond angle in the nitro derivatives **1c,e,f** varies from 119.4° to 122.2°; in **2c,e,f**, it varies from 127.7° to 121.8°; in **3c,e,f**, from 125.1° to 127.5°; in **4c,e,f**, from 123.7° to 125.0°; and in **5c,e,f**,

Fig. 4. Spatial structure of the N,N'-dinitro-5,6-dioxofurazano[3,4-*b*]piperazine molecule **4f**.

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Fig. 5. Spatial structure of the N,N'-dinitro-5,6-dihydroximinofurazano[3,4-*b*]piperazine molecule **5f**.

from 123.3° to 124.1°. These data may be used in quantum-chemical calculations of the spatial structure and estimation of some physicochemical properties of similar compounds without carrying out the procedure for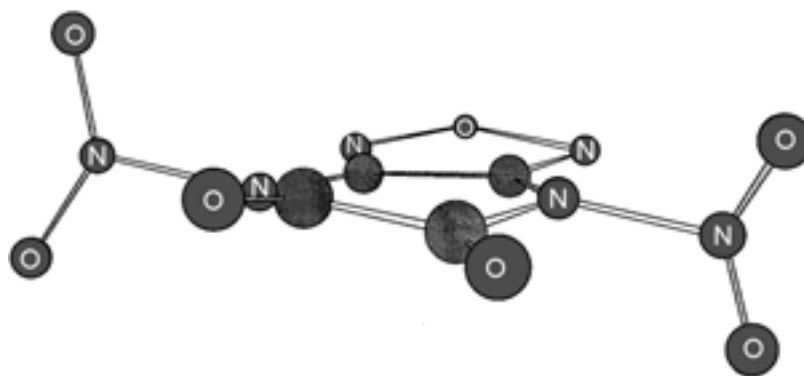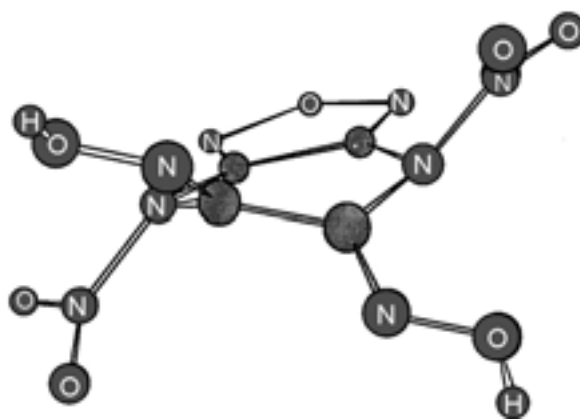 full optimization of the geometric parameters, which considerably shortens the calculation time. We note that varying the substituents (H, NO, NO_2) on the nitrogen atoms of the piperazine ring does not affect the bond lengths and bond angles of the heterocyclic skeletons of the molecules (Fig. 6).

Comparing the results of optimization of the geometric structure of the studied compounds, we can conclude that the *chair* conformation is most favorable for the piperazine moiety. Upon annelation with a furazan ring, the piperazine ring is flattened.

In Fig. 6, we show the average calculated values of the intramolecular parameters of the base skeletons of molecules in series **1-5**.

ELECTRONIC STRUCTURE OF THE COMPOUNDS

We carried out quantum-chemical calculations of the electronic structure parameters of the compounds: the charges on the ring nitrogen atoms, the dipole moments of the molecules, the ionization potentials, the energies of the frontier molecular orbitals (HOMO and LUMO) and the energy gap between them (Δ), and also the enthalpies of formation for the compounds in the gas phase and in the solid phase (Table 2).

From the results obtained it follows that introducing nitroso groups into the molecules of the investigated compounds increases the electron density on the N atom of the piperazine ring. In compounds of the series under consideration, the "increment" in electron density on the ring N atom compared with the electron density of the corresponding atom in piperazine (**1a**) on the average is 0.080 in **1**; 0.082 for series **2**; 0.097 for **3**; 0.023 for **4**; and 0.048 in the compounds of series **5**. Introducing nitro groups leads to an increase in the negative charge on the nitrogen atom bonded to it by 0.026 in compounds **1** and by 0.013 in **4**. For compounds in the remaining series, however, we observe a decrease in the charge on this atom: by 0.013 in series **2**, by 0.027 in **3**, and by 0.035 in compounds **5**.

Annelation of mononitroso and dinitroso derivatives of piperazine **2c,e,f** with the acceptor furazan ring leads to delocalization of the negative charge on the nitrogen atom of the piperazine ring and a decrease in the charge by 0.077 on the average. For mononitro derivatives, this decrease is 0.125, while in dinitro derivatives it is 0.110. Going to bisfurazanopiperazines **3** decreases the negative charge on the nitrogen atom of the piperazine ring in the nitroso compounds by another 0.086 compared with the corresponding compounds in series **2**, and by 0.114 in the nitro derivatives.
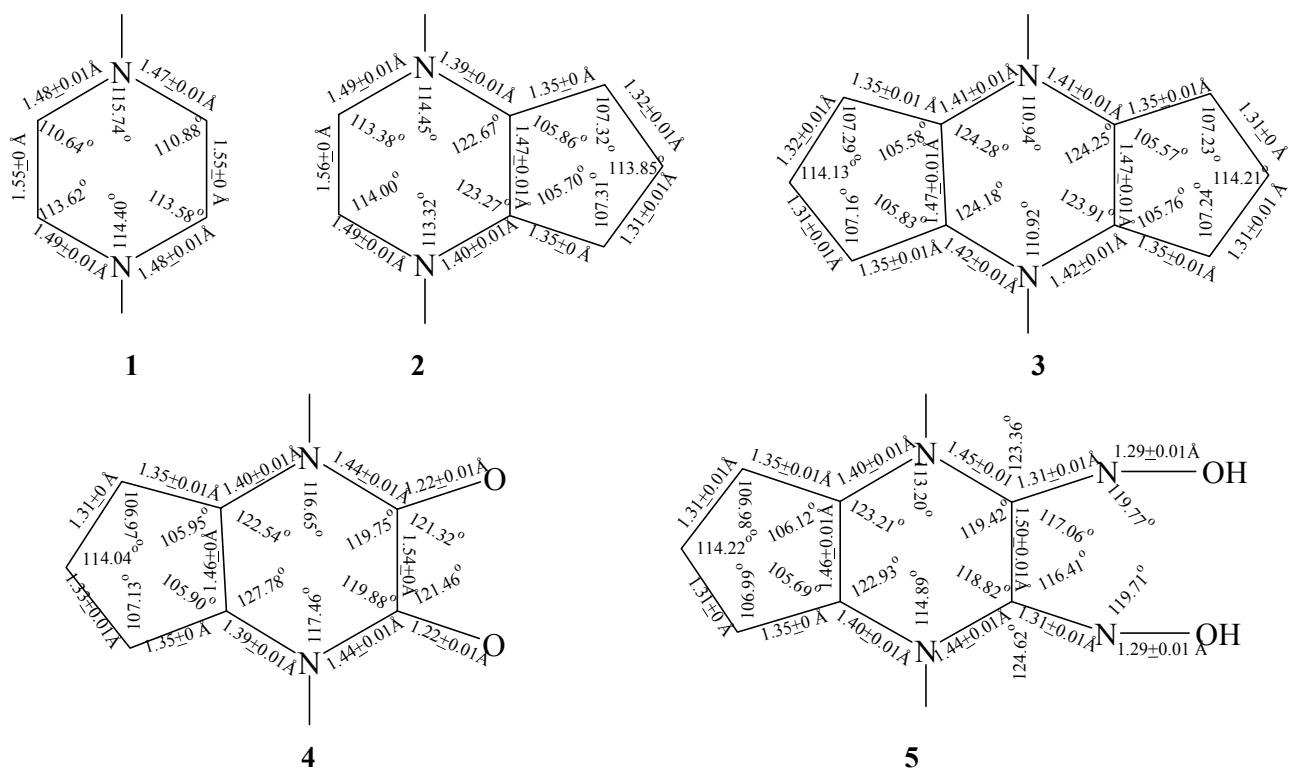
Fig. 6. Average values of the bond lengths and bond angles for the molecules in compounds **1-5**.

Introducing carbonyl groups into the piperazine ring of piperazinofurazans **2** increases the electron density on the nitrogen atom of the piperazine ring for both the mononitroso and dinitroso derivatives by 0.010, while for the mononitro and dinitro derivatives (series **4**), the increment is 0.096.

The electron density on the piperazine nitrogen atom in dihydroximines **5** is lower than in compounds of group **2**: 0.034 lower for nitro derivatives, and 0.041 lower for nitroso derivatives.

Let us consider the calculated values of μ as an integral characteristic of the polarity of the molecules. Introducing one NO or NO_2 group increases the dipole moment of the molecules (Table 2); an exception is compounds **2b** and **3b** (MNDO calculations). Introducing two identical substituents (either nitro or nitroso groups) lowers the μ of the molecules (except for compounds **4d,f** and **5d**).

According to the results obtained, diketones **4** are less polar than piperazines **1**; dioximes **5** are less polar than monoannelated compounds **2** but more polar than diannelated compounds **3**.

The results of calculations of the ionization potentials, the frontier molecular orbitals (HOMO and LUMO) and the energy gap (Δ) between the MOs (Table 2) suggest that condensation of the piperazine ring with a furazan ring does not affect the ionization potential but decreases Δ between the frontier orbitals in the nitroso derivatives by 1.210 according to MNDO calculations and by 0.896 eV according to PM3 calculations. In the nitro derivatives, Δ is equal respectively to 1.044 eV and 1.026 eV. Introducing a second furazan ring additionally enhances this effect on the average by 0.542 eV (MNDO) and 0.706 eV (PM3).

For dioxo derivatives **4**, Δ between the HOMO and LUMO is less than Δ in furazano[3,4-*b*]piperazines **2** on the average by 1.287 eV (MNDO) and 1.214 eV (PM3), while for dihydroximines it is 1.398 eV lower (MNDO) and 1.330 eV lower (PM3). These data may be used for analysis of the reactivity of the studied compounds in charge-controlled and orbital-controlled reactions.

THERMOCHEMICAL CHARACTERISTICS OF PIPERAZINE DERIVATIVES AND THEIR RELATION TO THE STRUCTURE OF THE COMPOUNDS

Chemical bond strength. To estimate the thermochemical characteristics of the piperazine derivatives, we calculated the enthalpies of formation and also the strength indices [36, 37] of the N–N bond, reflecting changes in the relative thermodynamic stability of the compounds upon structural changes in the molecules.

Thermal decomposition of most N-nitramines [13-15] and N-nitrosamines [15, 16] begins with homolytic breaking of the N–N bond, so we specifically considered this bond. The indices for the change in strength of the N–N bond in nitro and nitroso derivatives **1-5** were calculated using the formula:

$$i_{N–N} = \frac{E_{N–N} - E_{N–N}\,(\text{reference})}{E_{N–N}\,(\text{reference})} \times 100\%,$$

where $E_{N–N}$ is the two-center component of the total chemical bond energy [23]. As the "reference" (0%) we selected the strength of the N–N bond in N-nitropiperazine (**1c**).

The calculation results (Table 1) suggest that N-nitroso derivatives are more stable than the corresponding N-nitro derivatives. In compounds **1-5**, the strongest bond is the N–N bond in monocyclic piperazines (series **1**). Upon annelation with a furazan ring, the $N–NO_2$ and N–NO bonds become weaker (series **2**), an effect which is even more appreciable when a second furazan ring is introduced (series **3**). Such a change in the N–N bond strength when acceptor furazan moieties are introduced into the system can be explained by delocalization of electrons from the unshared electron pairs of the nitrogen atoms of the piperazine ring.

Analysis of the calculations of the N–N bond strength indices in compounds of groups **4** and **5** indicates that the strength of the bond between the NO group and the ring N atom is higher than the strength of the analogous bond with the NO$_2$ group. Mononitroso and dinitroso derivatives of series **4** are less stable than compounds in series **5**. This dependence is inverted for mononitro and dinitro derivatives.

Enthalpies of formation (ΔH_f^0). As indicated above, the enthalpies of formation for the compounds in the gas phase were estimated by the semiempirical PM3 method, and in the solid phase it was estimated using additive schemes [25-27].

Comparing the results of the ΔH_f^0 calculations (Table 2), we may note that on going from the compounds in series **1** to the compounds in series **2**, i.e., upon condensation with a furazan ring, both for the mononitroso and mononitro derivatives of piperazine we observe an increase in ΔH_f^0 by about 46-60 kcal/mol (in the gas phase) and 65-66 kcal/mol (in the solid phase). Introducing a second furazan moiety into the molecule additionally increases ΔH_f^0 by 78-80 kcal/mol (for the gas) and 65 kcal/mol (for the solid phase). For the dinitroso derivatives of piperazine, the increase in enthalpy of formation for each annelation with a furazan ring is 82-84 kcal/mol for both the gas and the solid. For the dinitro derivatives of piperazine, the analogous increment is even higher: up to 100 kcal/mol in the solid phase, and in the gas phase ΔH_f^0 increases by 117 kcal/mol when the first furazan ring is introduced, while upon condensation with the second furazan moiety the increment in the enthalpy of formation is 57 kcal/mol. Introducing carbonyl substituents into the compounds of series **2** lowers their enthalpies of formation both in the gaseous state and in the solid state over a broad range: from 23 to 106 kcal/mol (gas) and from 80 to 134 kcal/mol (solid phase). Modification of furazano-[3,4-*b*]piperazines **2** to form the dihydroximines of series **5** increases the enthalpy of formation for the mononitroso and mononitro derivatives by 18 kcal/mol (gas) and 24-28 kcal/mol (solid phase). In the dinitroso derivatives, the increase in ΔH_f^0 for the solid phase is ~10 kcal/mol, while for the gas phase the increase is 20 kcal/mol. The enthalpy of formation of the dinitro derivatives in the solid phase is virtually unchanged, while in the gas phase it is decreased by 7 kcal/mol.

Thus the enthalpy of formation for N-nitro derivatives in series **1-5** is lower than for the corresponding N-nitroso derivatives. Introducing a second NO group into the molecule of the mononitro derivative increases the enthalpies of formation for compounds **1-5**. These results on the whole are consistent with some of the available experimental data [15, 20].

Enthalpies of reaction for homolytic decomposition (ΔH_r). For a comparative estimate of the thermodynamic stability of the compounds, we considered the enthalpies of reaction for their homolytic decomposition, calculated by the density functional DFT B3LYP method in a 6-31 G* basis:

$$\Delta H_r = \Sigma \Delta H^0_{\text{products}} - \Sigma \Delta H^0_{\text{starting materials}}$$

For neutral molecules, the calculations were performed based on the restricted Hartree–Fock method (RHF), and for radicals we used the unrestricted Hartree–Fock method (UHF) [38]. As the most probable decomposition route, we selected homolytic breaking of the N–N bond to form two radicals [15]. The decomposition reactions and their corresponding ΔH_r values for piperazine derivatives **1** are shown in Scheme 1.

For compound **1f**, the experimental value [39] for the enthalpy of reaction for breaking of the N–N bond is 38.2 kcal/mol, which is close to our calculated value ($\Delta H_r = 40.69$ kcal/mol).

Nitro derivatives of piperazine are less stable (reactions (3), (4), Scheme 1) than their nitroso analogs (reactions (1), (2)). The difference between the enthalpies of reaction for homolysis is ~2 kcal/mol. N-Nitropiperazine (**1c**) and compound **1f** are not very different in stability, which is also the case for nitroso derivatives **1b** and **1d**. For N-nitroso-N'-nitropiperazine (**1e**), in principle two decomposition variants are possible (reactions (5) and (6), Scheme 1). The data represented in Scheme 1 show that detachment of the NO$_2$ group is most likely.
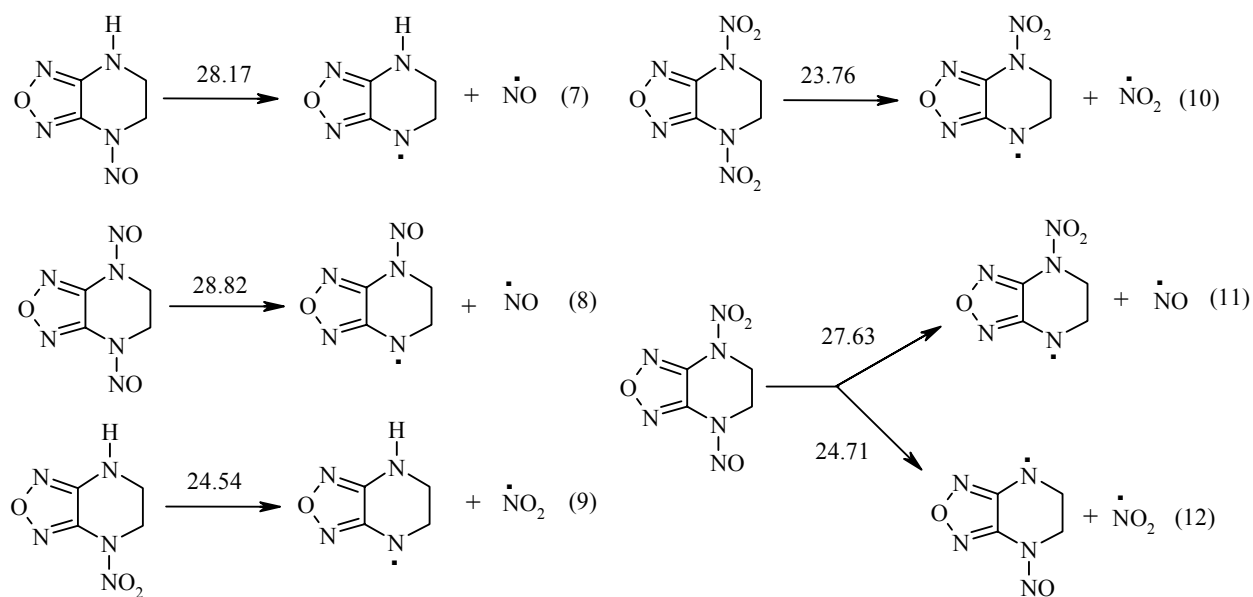
Scheme 1*
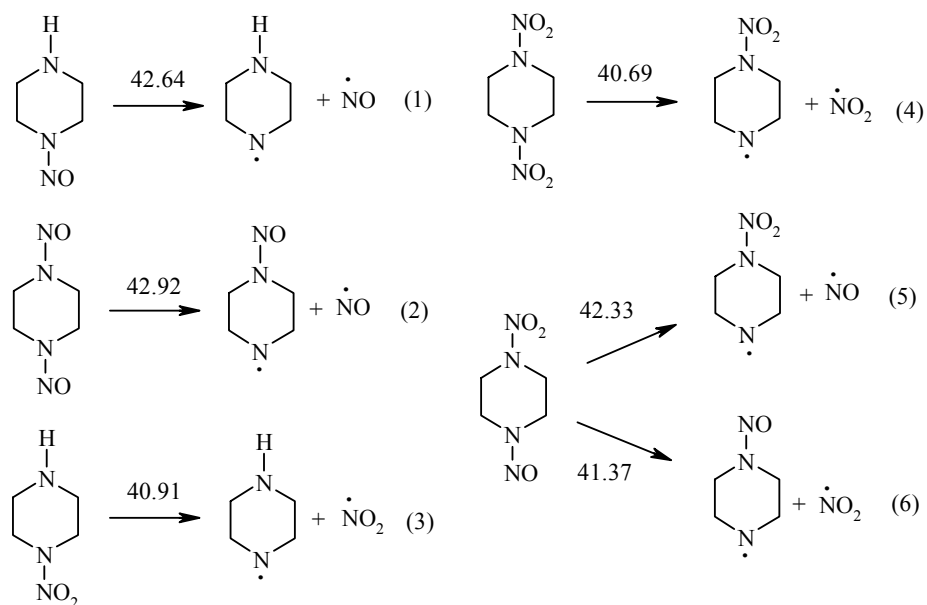
The decomposition routes for derivatives of furazanopiperazine **2** are presented in Scheme 2.

The difference between the enthalpies of reaction for decomposition of nitroso and nitro derivatives of furazano[3,4-*b*]piperazine is ~4 kcal/mol. As for the piperazine derivatives, the nitro derivatives in this series are less stable than the nitroso derivatives. For N-nitroso-N'-nitrofurazano[3,4-*b*]piperazine (**2e**), the most favorable decomposition involves detachment of a nitro group (reactions (11) and (12), Scheme 2). We note that introducing a furazan moiety into the piperazine derivatives lowers the stability of the nitroso derivatives by a factor of 1.5, and lowers the stability of the nitro derivatives by a factor of 1.7.
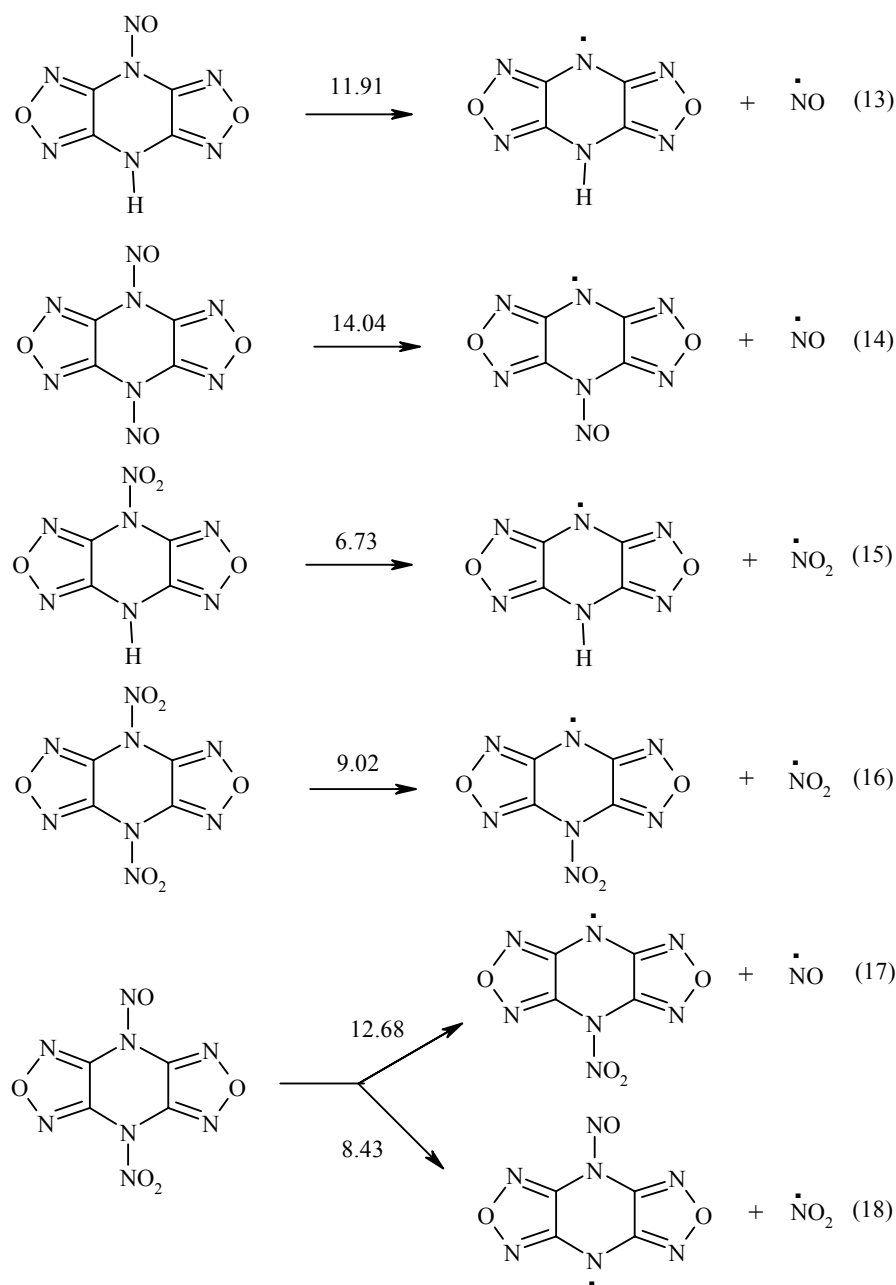
Scheme 2

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* Here and in the following, the values given on the schemes above the arrows are measured in kcal/mol.

The likely initial reactions for decomposition of the compounds in group **3** (derivatives of bisfurazano[3,4-*b*;3',4'-*e*]piperazine) and the enthalpies characterizing them are presented in Scheme 3.

Scheme 3

11.91 (13)

14.04 (14)

6.73 (15)

9.02 (16)

12.68 (17)

8.43 (18)

For compounds **3**, we observe an appreciable difference in thermodynamic stability between the nitro and nitroso derivatives, and the latter compounds are more stable. The difference between the enthalpies in the reactions of decomposition of these compounds is ~5 kcal/mol. Thus N-nitrosobisfurazano[3,4-*b*;3',4'-*e*]-piperazine (**3b**) is more stable (ΔH_r = 11.91 kcal/mol) than the corresponding mononitro derivative **3c** (ΔH_r = 6.73 kcal/mol). N,N'-Dinitrosobisfurazano[3,4-*b*;3',4'-*e*]piperazine (**3d**) (ΔH_r = 14.04 kcal/mol) is more

stable than the dinitro derivative (**3f**) with $\Delta H_r = 9.02$ kcal/mol. For N-nitro-N'-nitrosobisfurazano[3,4-*b*;3',4'-*e*]-piperazine (**3e**), initial breaking of the N–NO$_2$ bond is most likely (reaction (18), Scheme 3).

Introducing a second furazan moiety reduces the stability of N-nitroso, N,N'-dinitroso, and N,N'-dinitro derivatives by a factor of 2-2.5. The enthalpy of reaction for homolytic decomposition of N-nitrobisfurazano[3,4-*b*;3',4'-*e*]piperazine **3b** (reaction (15), Scheme 3) is a factor of 3.6 lower than the enthalpy of reaction for the corresponding derivative of N-nitrofurazano[3,4-*b*]piperazine **2c** (reaction (9), Scheme 2).

The results of estimation of the enthalpies ΔH_r for compounds **4** (Scheme 4) show that N-nitroso-5,6-dioxofurazano[3,4-*b*]piperazine (**4b**) is more stable ($\Delta H_r = 23.82$ kcal/mol) than the corresponding N-nitro derivative (**4c**) with $\Delta H_r = 20.35$ kcal/mol.

Scheme 4
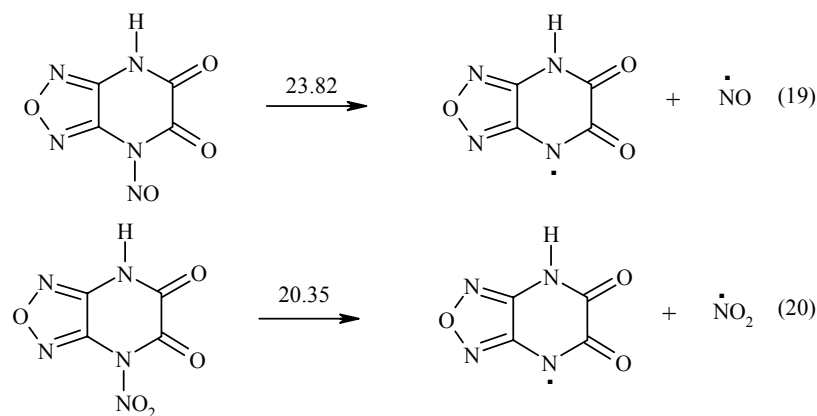
As in the case of the compounds in series **1-3**, the nitroso derivatives of series **4** are more stable than the nitro derivatives. We note that introducing two carbonyl oxygen atoms into the structure of the nitro and nitroso derivatives of furazanopiperazine **2** decreases the stability of the corresponding molecules **4** in decomposition reactions, but not so much as introducing a second furazan ring (compounds in series **3**).

Comparison of the results of calculations of the enthalpies of reaction for homolytic decomposition for compounds in series **5** and **3** allows us to conclude that introducing two NOH groups (instead of a furazan ring) into the molecules for nitro- and nitrosofurazanopiperazines decreases ΔH_r considerably. Thus compounds **5b** (Scheme 5, reaction (21)) and **5c** (reaction (22)) are less stable than the corresponding derivatives of bisfurazano[3,4-*b*;3',4'-*e*]piperazine (reactions (13) and (15), Scheme 3).
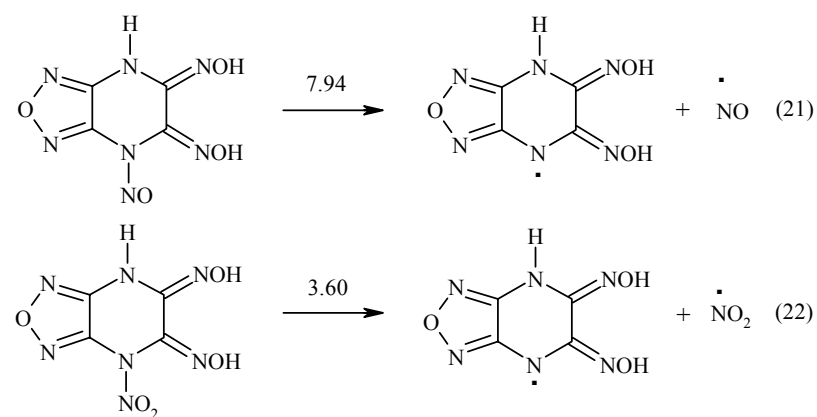
Scheme 5

Based on analysis of the first stage of the decomposition reaction for the studied compounds, we can conclude that introducing a furazan moiety into the system for nitro and nitroso derivatives of piperazine **1** (series **2**) decreases their thermodynamic stability in decomposition reactions. Annelation with a second furazan ring reduces the stability of these compounds even more.

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