ISSN 1070-4280 Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 2, pp. 278–287. © Pleiades Publishing, Inc. 2006.
Original Russian Text © V.V. Mezheritskii, L.G. Minyaeva, O.M. Golyanskaya, R.B. Tyurin, O.Ya. Borbulevich, G.S. Borodkin, A.N. Antonov, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, no. 2, pp. 293–302.

Oxidative Transformations of Peridazines

V.V. Mezheritskii[1], L.G. Minyaeva[1], O.M. Golyanskaya[1], R.B. Tyurin[1], O.Ya. Borbulevich[2], G.S. Borodkin[1], and A.N. Antonov[1]

[1]*Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don, 344090 Russia*
e-mail: mezher@ipoc.rsu.ru
[2]*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA*
e-mail: oborbulevych@yahoo.com

Received December 27, 2004

Abstract—Reactions of peridazines (1*H*-1,2-diazaphenalenes) with electron-donor reagents (quinones, potassium ferrocyanide) involve multistage oxidative transformations resulting in products of dimarization and (or) dehydration.

DOI: 10.1134/S1070428002120229

peri-Annelated pyridazine derivatives **I** discovered in 1971 [1] which in keeping with the IUPAC nomenclature should be named 1*H*-benzo[*de*]cinnoline derivatives or 1*H*-naphtho[1,8-*de*]pyridazine derivatives were designated by Lacy and Smith as 1*H*-1,2-diazaphenalenes (from phenalene hydrocarbon). In this paper we introduce the term "peridazine" by analogy with perimidine (**II**) (1*H*-1,3-diazaphenalene, or by the IUPAC nomenclature, 1*H*-benzo[*de*]quinazoline or 1*H*-naphtho[1,8-*de*]pyrimidine) [2]. Then acenaphthene and acenaphthylene derivatives of this heterocyclic system **III** and **IV** should be called respectively "aceperidazine" and "aceperidazylene" by analogy with aceperimidine and aceperimidilene [3, 4]. We believe that the introduced nomenclature will significantly simplify the discussion of the material treated in this paper.

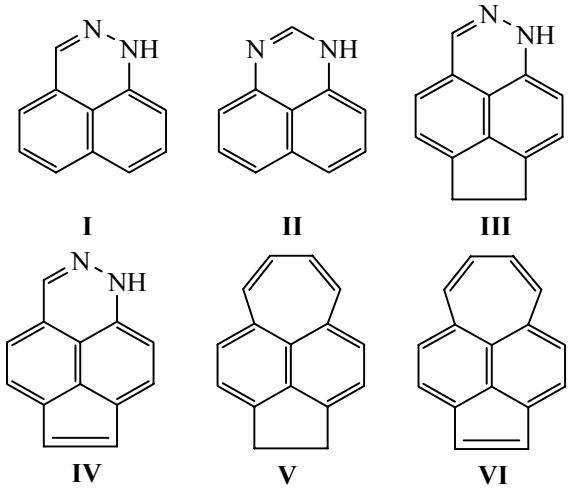


Fig. 1. Structural formulae of *peri*-annelated diazines and their carbocylic isoelectronic analogs

It is reasonable to compare the pair of the *peri*-annelated heterocyclic systems aceperidazine **III**–aceperidazylene **IV** with a pair of isoelectronic hydrocarbons: acepleiadiene **V**–acepleiadylene **VI** (Fig. 1).

The nomenclature and some explanations regarding these hydrocarbons we have taken from the book of O.E. Shelepin [5]. Hydrocarbons **V** and **VI** were synthesized and investigated as early as 1956 [6]. It was observed that the seven-membered ring of acepleiadiene **V** possessed a pronounced divinyl character, and that the aromaticity was characteristic of acepleiadylene **VI**. The predominant role of 14p-electron ring-current and a specific feature of the internal double bond occupying the nonbonding orbital in the latter compound were also indicated [7, 8]. These comparisons corrected for the difference of aromatic hydrocarbons from heteroaromatic [9] are apparently valid also for the *peri*-annelated diazines **III** and **IV**. The first representatives of heteroaromatic compounds with the topology of the π-system like in peridazylenes **IV** were prepared by A.F.Pozharskii *et al.* [3, 4] in the perimidime series. Later [10] some reactions of these compounds were studied demonstrating the features of the chemical behavior of the new heteroaromatic systems.

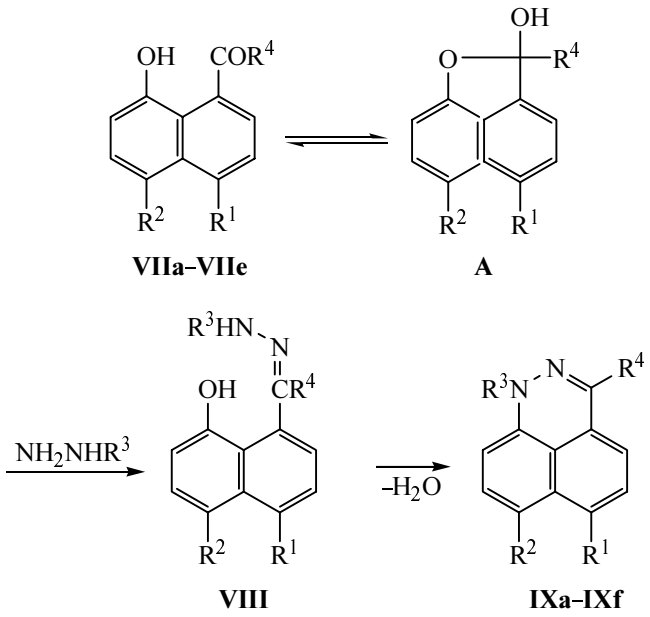
The compounds of the peridazine series possess exclusively high electron-donor ability and thus they are interesting objects both for theoretical and experimental research in the fields of quantum-chemical calculations, fine organic synthesis and mechanisms of ion-radical and

free-radical reactions. They also may provide new types of efficient antioxidants with a wide range of biological activity. The data on synthethic methods and properties of peridazines are compiled in reviews [11, 12].

It was shown formerly [13, 14] that the treatment of peridazines with one-electron acceptors ($AgClO_4$) easily afforded stable crystalline salts (perchlorates) of cation-radicals. The goal of the present study consisted in the investigation of peridazine reactions with oxidants like quinones and potassium ferrocyanide. The peridazine derivatives **IX** required for this work were prepared by the previously developed procedure [1, 15] based on the reaction of the *peri*-hydroxy-substituted ketones **VII** with hydrazine and methylhydrazine (Scheme 1).

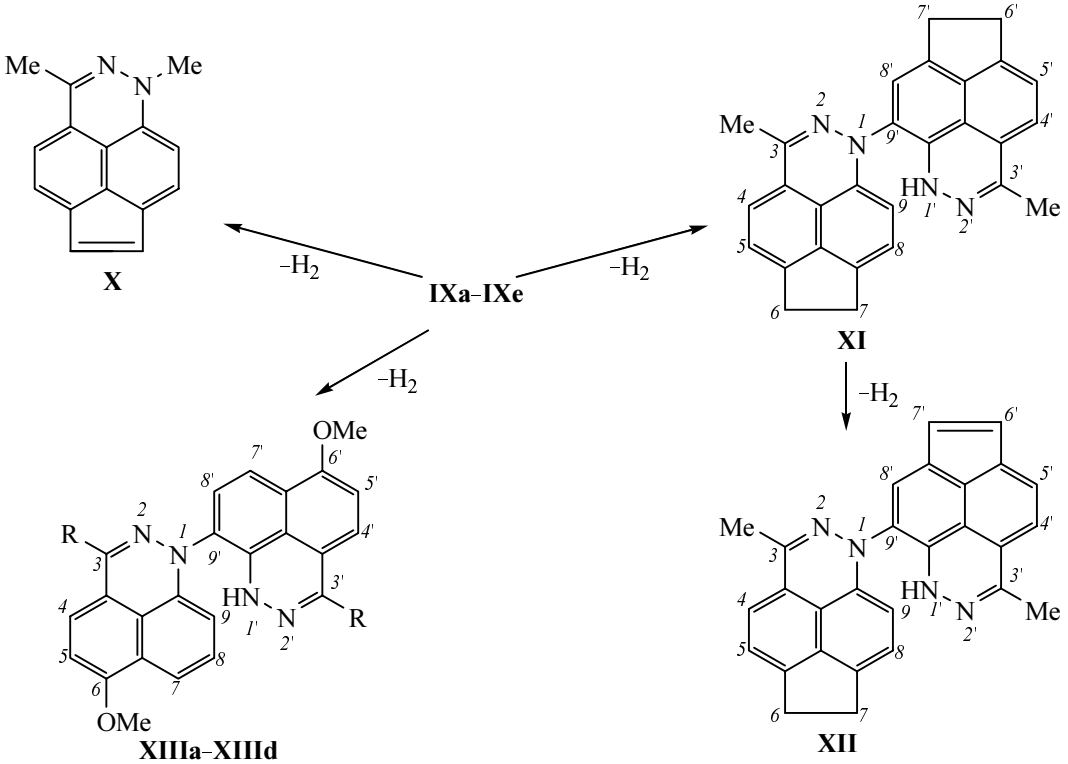
As shown before [15], in the first stage of this process arose hydrazones **VIII** that if required might be isolated and transformed into the corresponding peridazines **IX** by heating in alcohol. Compounds **IXe** and **IXf** were prepared for the first time, and the syntheses of the rest peridazines **IXa–IXd** were described in [15–17]. It was observed that the formation of peridazines **IXe** and **IXf** from 5-acetyl-6-hydroxyacenaphthene (**VIIe**) and hydrazine or methylhydrazine required significantly longer heating in alcohol than in preparation of 1-acetyl-8-

Scheme 1.



VII, R^1 = MeO, R^2 = H, R^4 = Me (**a**), Et (**b**), Ph (**c**); R^1 = R^2 = H, R^4 = $N(CH_2CH_2)O$ (**d**); R^1–R^2 = CH_2–CH_2, R^4 = Me (**e**); **IX**, R^1 = MeO, R^2 = R^3 = H, R^4 = Me (**a**), Et (**b**), Ph (**c**); R^1 = R^2 = R^3 = H, R^4 = $N(CH_2CH_2)O$ (**d**); R^1–R^2 = CH_2–CH_2, R^4 = Me, R^3 = H (**e**), Me (**f**).

Scheme 2.



R = Me (**a**), Et (**b**), Ph (**c**), $N(CH_2CH_2)_2O$ (**d**).

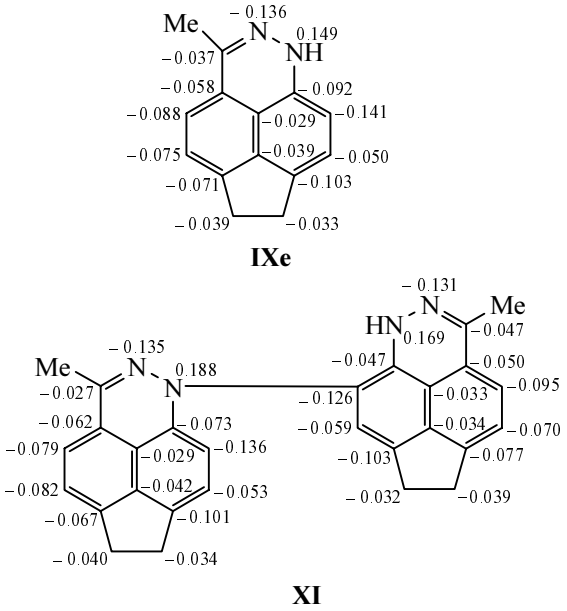


Fig. 2. Quantum-chemical calculations by PM3 method of the electron density distribution in the molecules of compounds **IXe** and **XI**.

hydroxy- or 1-acetyl-8-hydroxy-4-methoxynaphthalenes. This is apparently due to the difficulty in the closire of the second five-membered ring in formation of cyclic tautomer **A**, the indispensable precursor of hydrazones **VIII**. At the use of ethylhydrazine instead of methylhydrazine we completely failed to obtain from the *peri*-hydroxyacetoacenaphthone **VIIe** either the corresponding hydrazone **VIII** or aceperidazine (**IX**, R = Me, R^3 = Et, R^1–R^2 = CH_2–CH_2) which is difficult to comprehend to be caused by the influence of the electronic and sterical factors.

The reaction with oxidants proceeds significantly different in N-methyl-substituted peridazines or peridazines lacking a substituent at the "pyrrole type" nitrogen. The treating with 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) of 1,3-dimethylaceperidazine (**IXf**) furnished 1,3-dimethylaceperidazylene (**X**), the first representative of a new *peri*-annelated heteroaromatic system with a 14π-electron ring current.

It is interesting to follow the changes in the ^{1}H NMR spectrum in going from 1,3-dimethylaceperidazine (**IXf**) to 1,3-dimethylaceperidazylene (**X**). In the spectrum of the former the signals of the aromatic protons are located in the region from 5.9 to 7.0 ppm, whereas in the spectrum of the latter these signals shift downfield by 1.4 ppm and appear in the range from 7.1 to 8.5 ppm. This fact unambiguously evidences the aromatization of the heterocyclic system on appearance of a vinyl "bridge" in the peri-positions opposite to the heterocycle. The increase in the diamagnetic ring current as manifestation of aromaticity is also evidenced by the downfield shift of 0.96 and 0.80 ppm of the proton signals from the methyl groups attached to positions 1 and 3 respectively in the spectrum of 1,3-dimethylaceperidazylene (**X**) as compared with that of 1,3-dimethylaceperidazine (**IXf**). The protons of the vinylene "bridge" of aceperidazylene **X** appear in the range 7.63–7.80 ppm, but their spin-spin coupling constant is notably smaller (*J* 4.1 Hz) than that of the protons of the naphthalene core (J 7.5 and 8.1 Hz). In the ^{1}H NMR spectrum of aceperidazine **IXf** the characteristic signals are those of naphthalene protons at C^5 and C^8 observed as doublets of triplets due to the coupling with the aromatic protons on C^4 and C^9 and with the protons of the bimethylene moiety.

The peridazines with a free position *1* behave different at oxidation. In particular, the oxidation of 3-methylaceperidazine **IXe** depending on the oxidant (quinones, potassium ferrocyanide), composition of the medium, and the reagents ratio furnished either dimer **XI**, the product of partial dehydration of the latter **XII**, or a mixture of both. In reaction of 3-methylaceperidazine **IXe** with equimolar quantity of 3,5-di-*tert*-butyl-1,2-benzoquinone in ether or acetonitrile dimer **XI** was obtained in a low yield, whereas at excess *ortho*-quinone the dehydration occurred of one of the acenaphthene fragments of the dimer into acenaphthylene giving compound **XII**. The oxidation of 3-methylaceperidazine **IXe** with the potassium ferrocyanide gave rise to non-separable mixture of oxidation products **XI** and **XII** in a changeable ratio; their identification was easily performed by means of ^{1}H NMR spectra.

The dimeric structure of compound **XI** is proved by the presence in its mass spectrum of peaks from a monovalent (*m/z* 414, I_{rel} 100%) and divalent (*m/z* 407, I_{rel} 35%) molecular ions. In the ^{1}H NMR spectrum apart from two three-proton singlets of magnetically non-equivalent 3- and 3'-methyl substituents and the eight-proton signal of two bimethylene groups appeared the aromatic multiplet consisting of six one-proton doublets and one-proton singlet, and also the one-proton singlet of NH group disappearing on deuteration. The comparison of ^{13}C NMR spectra registered with and without decoupl-ing from protons shows the presence of 13 carbons linked to protons and 15 carbons with no protons that does not contradict the structure of dimer **XI**. The accurate assignment of signals in the NMR spectra was done taking into account the coupling constants and the calculation of the electron densities on the carbon atoms in the 3-methylaceperidazine and its dimer (Fig. 2).

The reaction of 3-methylaceperidazine **IXe** with excess 3,5-di-*tert*-butyl-1,2-benzoquinone in ether as already mentioned was completed by formation of compound **XII** containing aceperidazine and aceperidazylene fragments. The structure of the compound was established from the ^{1}H NMR spectrum, COSY spectrum, and mass spectrum.

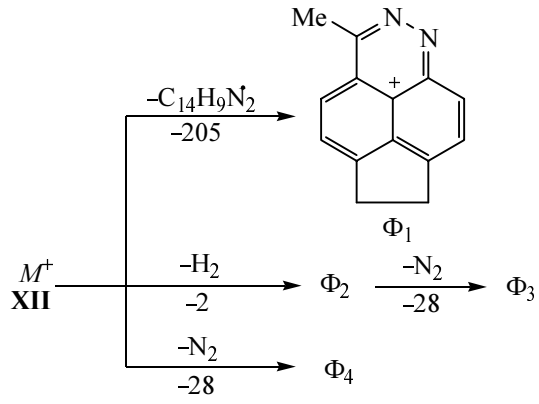
The dimer structure of compound **XII** is confirmed by the presence of a stable molecular ion M^+ (*m/z* 412, I_{rel} 100%) and by the character of its fragmentation whose most informative paths lead to cation Φ_1 (*m/z* 207, I_{rel} 50%), the product of bimethylene moiety dehydration Φ_2 (*m/z* 410, I_{rel} 80%), and fragment ions Φ_3 (*m/z* 382, I_{rel} 60%) and Φ_4 (*m/z* 384, I_{rel} 70%) arising through nitrogen molecule liberation.

Inasmuch as in the dimer molecule **XII** are linked the aceperidazine (pseudoaromatic) and aceperidazylene (heteroaromatic) fragments its ^{1}H NMR spectrum in the region of aromatic protons is actually a superposition of the spectra from diazines **IXf** and **IXe** and from **X,** and it includes the range from 5.84 to 8.46 ppm. In the ^{1}H NMR spectrum of dimer **XII** alongside the signals of two magnetically nonequivalent methyl groups (two three-proton singlets) and that of the bimethylene fragment (two broadened two-proton triplets, cf. the spectra of compounds **IXf** and **IXe**) appear two one-proton doublets of triplets (H^5 and H^8, cf. the spectra of compounds **IXf** and **IXe**), two one-proton doublets (protons H^4 and H^9), four one-proton doublets (protons H$^{4'}$, H$^{5'}$ and H$^{6'}$, H$^{7'}$, cf. the spectrum of compound **X**) with the characteristic coupling constants, one-proton singlet (proton H$^{8'}$), and downfield (10.7 ppm) singlet of N^{1}H evidencing the presence of an intramolecular hydrogen bond. This pattern of the ^{1}H NMR spectrum of dimer **XII** compared with the spectra of aceperidazines **IXf** and **IXe** and of aceperidazylene **X**, and the accounting for the mass spectra and the calculation of the electron densities on the skeleton atoms of the heterocyclic system (Figs. 2 and 4) made it possible to unambiguously elucidate the junction positions of the fragments and to assign the proton signals both in the spectrum of dimer **XII** and compounds **IXf** , **IXe** and **X**.

The accuracy of assignment of proton signals in the spectrum of dimer **XII** was proved also by the 2D (COSY) spectrum where the coupling of protons is clearly revealed by the corresponding cross-peaks (Fig. 3).

According to the quantum-chemical calculations (Figs. 2 and 4) diazines **IXf** , **IXe** and **X** belong to the so-called π-excessive heterocycles [9] since all the atoms

Scheme 3.



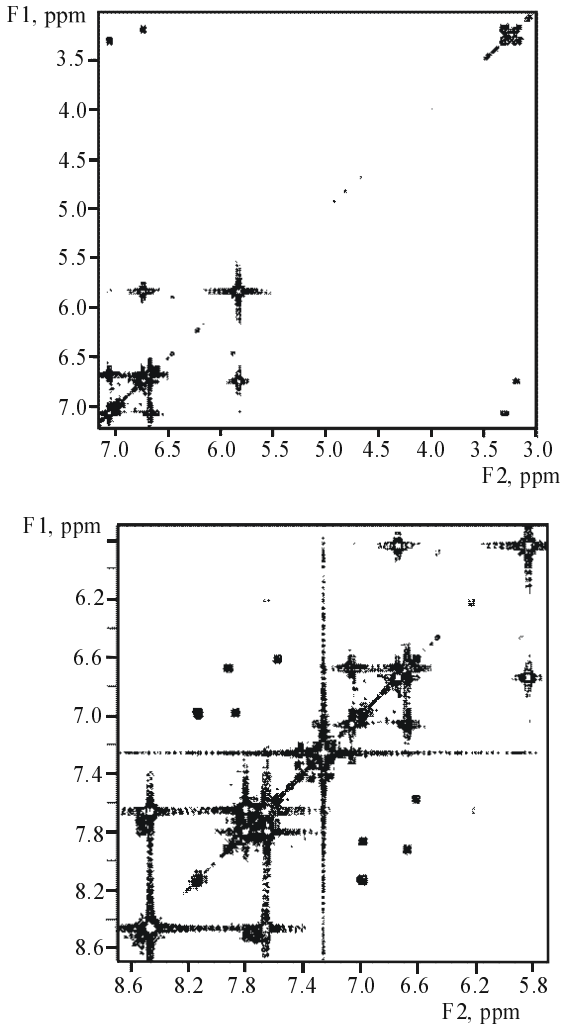


Fig. 3. ^{1}H NMR 2 D spectrum (COSY) of dimer **XII**.

of the heterocyclic framework (except for the "pyrrole" type nitrogen in position *1*) are negatively charged, and this charge is essentially supplied by the electron-donor effect of the "pyrrole" heteroatom. The attention should

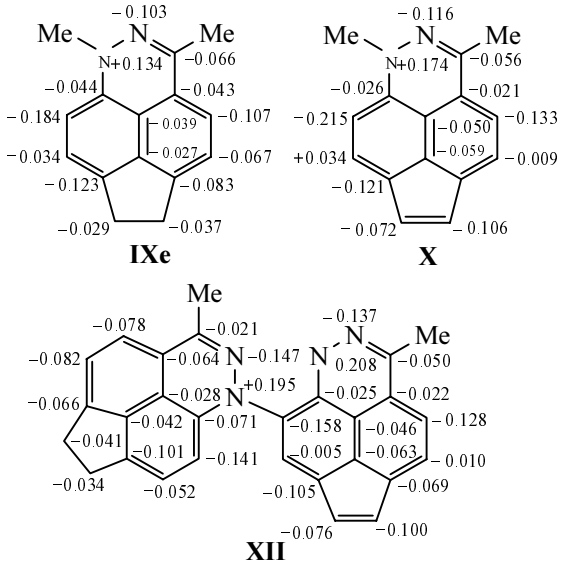


Fig. 4. Quantum-chemical calculations by PM3 method of the electron density distribution in the molecules of compounds **IXf**, **X**, and **XII**.

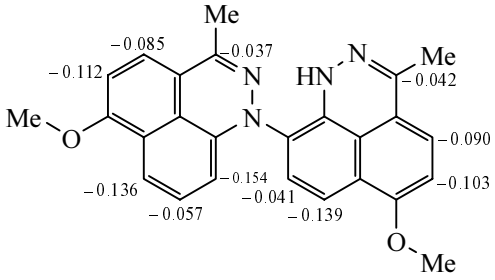


Fig. 5. Charge densities on the skeleton atoms of dimer **XIIIa** calculated by PM3 procedure.

be drawn to the negative charge on the atoms *6* and *7* of the "vinylene" bridge in aceperidazylene **X**; the charge is nearly three times greater than that on the atoms of the bimethylene group of aceperidazine **IXf** and **IXe**. The results of calculations suggest a high reactivity of these compounds with respect to electrophilic reagents, and the attack should be directed on the atoms in positions *2*, *4*, *6*, and *9* possessing the largest negative charge. The similar distribution of electron density is observed in the acenaphthene and acenaphthylene fragments of the molecule of dimer **XII**.

At treating with 3,5-di-*tert*-butyl-1,2-benzoquinone 6-methoxy-substituted peridazines **IXa–IXd** the fusion of two heterocyclic fragments also occurred affording dimers with a junction by the N^{1}–$C^{9'}$ bond **XIIIa–XIIId** (Scheme 2). Same as the majority of oxidations of organic compounds this process gives ambiguous results affording complex mixtures whose workup with the use of column chromatography furnished dimers **XIIIa–XIIId** in the yield varying in the range 20–30%.

The structure of dimers **XIIIa–XIIId** was established from spectral data. In the ^{1}H NMR spectra of compounds **XIIIa** and **XIIIb** the two upfield signals from 3- and 3'-alkyl substituents indicate their magnetic nonequival - ence. The pattern of aromatic protons signals is nearly the same for both compounds: two one-proton signals, namely, an upfield doublet (~6.1 ppm, H^{9}) and a triplet (~7.1 ppm, H^{8}), and also eight one-proton doublets in the range 6.5–7.3 ppm. The aromatic protons in the ^{1}H NMR spectrum of dimer **XIIIc** substituted with two phenyl groups in positions *3* and *3'* gave rise to a complex nineteen-proton multiplet in the region 6.2–7.8 ppm where only the upfield doublet at 6.2 ppm was clearly identified as belonging to H^{9}. The chemical shifts of protons from 6- and 6'-methoxy groups in dimer **XIIIa–XIIIc** coincide forming a single six-proton peak. The protons of the morpholine substituent in the ^{1}H NMR spectrum of compound **XIIIc** appeared in a strong field as a couple of broadened eight-proton signals, and the aromatic protons are observed as an eleven-proton multiplet (5.8–7.6 ppm). The protons of the NH groups in the spectra of dimers **XIIIa–XIIId** give a downfield singlet at 8.2–8.4 ppm disappearing on deuteration. We were guided in the assignment of proton signals by the values of charge density on the skeleton atoms of the *peri*-annelated heterocyclic fragments in the structure of dimer **XIIIa** (Fig. 5).

In the IR spectra of dimers **XIIIa–XIIIc** registered from mulls in the mineral oil we failed to detect the stretching vibrations bands of the N–H bond.

The structure of dimer **XIIIa** was proved by the X-ray diffraction analysis (Fig. 6).

Bond lengths and bond angles in compound **XIIIa** (Tables 1 and 2) are close to standard values [18]. Two heterocyclic fragments A and B fused by the C^{9A}–N^{1B} bond are virtually planar and orthogonal to each other. The angle between the planes going through all nonhydrogen atoms of the fragments A and B equals 85.96(6)°.

In the crystal of compound **XIIIa** form centrosymmetrical dimers (Fig. 7) owing to intermolecular hydrogen bond N^{1A}–H^{1A}···$N^{2A'}$ (–*x*, –*y* + 1, –*z* – 1) between the atoms of fragment A: N^{1A}···$N^{2A'}$ 3.126(5), H^{1A}···$N^{2A'}$ 2.49 Å, angle $N^{1A}H^{1A}$···$N^{2A'}$ 131°.

In the crystal compound **XIIIa** exists as a solvate with toluene of 2:1 composition, and the solvent is disordered by two position with occupancies of 0.5.

The first stage of all observed treansformations in all cases studied was an electron transfer from the peridazine to the oxidant yielding stable cation-radicals. The ease of formation of the latter is proved chemically by isolation stable cation-radical [13, 14], by spectral (the observation of ESR spectra of cation-radicals) [13, 14, 19], and electrochemical (polarography, voltammetry, electrolysis) [13, 20] methods.

The hypothetical mechanism of the oxidative dimerization of peridazines treated with *ortho*-quinones is presented in Scheme 4.

The established fact of dimers **XI** and **XIII** formation permits an assumption of the existence of associates of **A** type in the solutions of peridazines. The associates in reaction with quinone **B** may give ion-radical salts (**C** · 2**D**). The possibility of dimeric associates **A** formation is confirmed by the presence in crystals of centrosymmetrical dimers (Fig. 7). After a proton transfer from the associated cation-radical **C** to the anion-radical **D** the coupling of the unpaired electrons occurs followed by aromatization (**E**→**H**). The quinone is converted into a hydroquinone along the route **B**→**D**→**F**→**G**.

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometers Bruker DPX-250 (250 MHz) and Varian Unity-300 (300 MHz), internal reference HMDS. IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil. Mass spectra were measured on Finigan MAT INCOS-50 instrument (electron impact, ionizing voltage 70 V, direct admission of the sample into the ion source). The purification of compounds by column chromatography was carried out on aluminum oxide, eluents chloroform and ether. In the EXPERIMENTAL the names of compounds are given in keeping with the IUPAC nomenclature, and the names used in this paper are written in quotes.

X-ray diffraction study of compound XIIIa. The crystals were obtained by isothermal evaporation of the solution of compound **XIIIa** in toluene. Crystals $C_{26}H_{22}O_2N_4 \cdot 1/2C_7H_8$ (toluene) at 293(2) K monoclinic, *a* 18.194(4), *b* 13.616(3), *c* 10.091(2) Å, β 106.06(3)°, *V* 2402.3(8) Å^3, size of the crystal 0.4 × 0.3 × 0.2 mm, space group $P2_1/C$, *Z* 4, d_{calc} 1.289 g/cm^3, F(000) 978, μ 0.083 mm^{-1}.

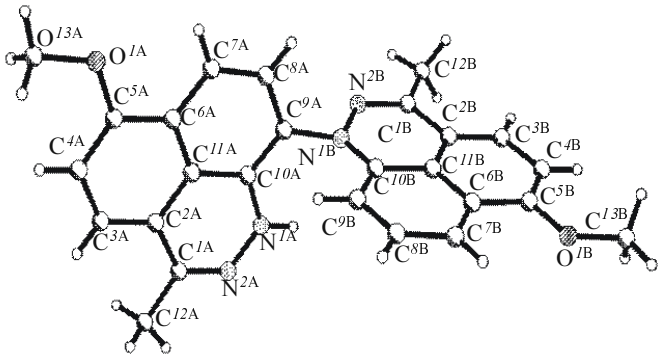


Fig. 6. General view of molecule **XIIIa**.

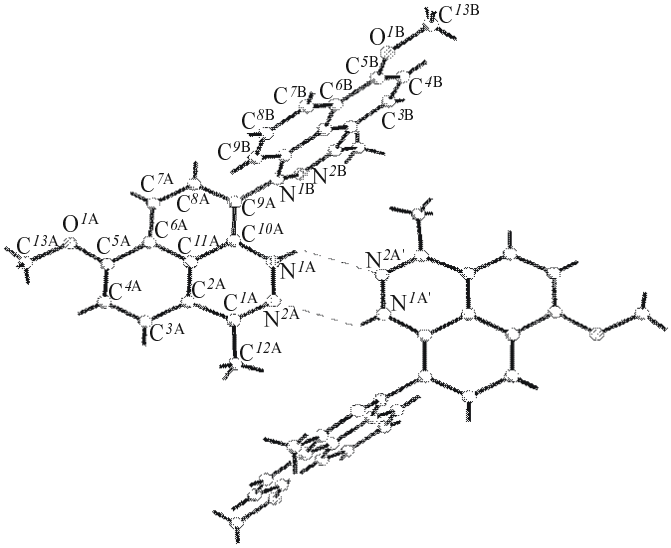


Fig. 7. Centrosymmetrical dimer of molecule **XIIIa** existing in the crystalline phase. Numeration is not given for atoms of the molecule obtained by the symmetry operation –*x*, –*y* + 1, –z – 1.

The intensities of 3963 reflections (R_{int} 0.099) were measured on an automatic four-circle diffractometer Enraf-Nonius CAD4 (β-filter, MoK_α-radiation, θ/2θ scanning, $2\theta_{max}$ 50°). The array of reflections obtained was subjected to a profile analysis along procedure [21] that significantly improved its quality.

The structure was solved by the direct method with the use of software package SHELXTL PLUS [22]. The positions of the hydrogen atoms were calculated geometrically and refined by the *rider* model with fixed $U_{iso} = nU_{eq}$ of the nonhydrogen atom linked to the given hydrogen (n = 1.5 for hydrogen in the methyl and carboxy groups, 1.2 for the rest of hydrogen atoms). In refining the disordered solvate toluene molecule the restriction were set for the following bond lengths: C(Ar)–C(Ar) 1.400(4) and C(Ar)–CH_3 1.475(4) Å [20]. The refinement

Scheme 4.

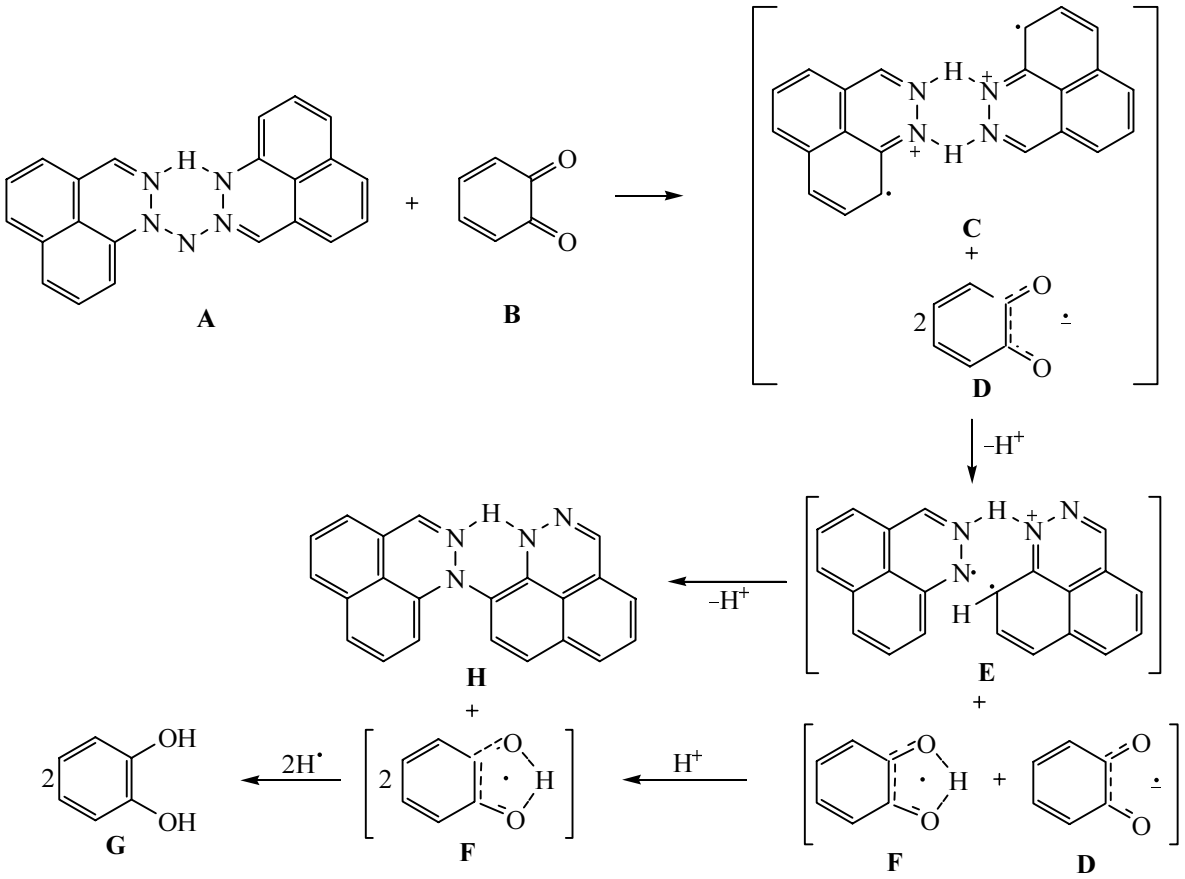


Table 1. Some bond lengths (*l,* Å) in compound **XIIIa**

Bond	*l*, Å	Bond	*l*, Å
N^{1A}–N^{2A}	1.366 (5)	N^{1B}–N^{2B}	1.376 (5)
N^{1A}–C^{10A}	1.383 (5)	N^{1B}–C^{10B}	1.394 (5)
N^{2A}–C^{1A}	1.289 (5)	N^{2B}–C^{1B}	1.295 (5)
O^{1A}–C^{5A}	1.371 (4)	O^{1B}–C^{5B}	1.366 (5)
O^{1A}–C^{13A}	1.435 (5)	O^{1B}–C^{13B}	1.439 (6)
C^{1A}–C^{2A}	1.468 (5)	C^{1B}–C^{2B}	1.467 (6)
C^{1A}–C^{12A}	1.497 (6)	C^{1B}–C^{12B}	1.475 (7)
C^{2A}–C^{3A}	1.367 (5)	C^{2B}–C^{3B}	1.384 (6)
C^{2A}–C^{11A}	1.422 (5)	C^{2B}–C^{11B}	1.404 (6)
C^{3A}–C^{4A}	1.397 (6)	C^{3B}–C^{4B}	1.400 (6)
C^{4A}–C^{5A}	1.368 (6)	C^{4B}–C^{5B}	1.370 (7)
C^{5A}–C^{6A}	1.415 (5)	C^{5B}–C^{6B}	1.442 (6)
C^{6A}–C^{7A}	1.404 (5)	C^{6B}–C^{7B}	1.399 (6)
C^{6A}–C^{11A}	1.416 (5)	C^{6B}–C^{11B}	1.422 (6)
C^{7A}–C^{8A}	1.350 (6)	C^{7B}–C^{8B}	1.383 (6)
C^{8A}–C^{9A}	1.398 (6)	C^{8B}–C^{9B}	1.367 (6)
C^{9A}–C^{10A}	1.360 (5)	C^{9B}–C^{10B}	1.375 (6)
C^{10A}–C^{11A}	1.415 (5)	C^{10B}–C^{11B}	1.421 (5)
C^{9A}–C^{1B}	1.448 (5)		

with respect to F^2 in the anisotropic approximation (343 parameters) for nonhydrogen atoms applying the least-squares full-matrix procedure to 3831 reflections was performed till R_1 0.0811 [for 1898 reflections with F>4σ(F)], wR_2 0.236, S 0.987. Some bond lengths and bond angles are presented in Tables 1 and 2.

3-Methyl-1*H*-acenaphtho[5,6-*de*]pyridazine (IXe), "3-methylaceperidazine". A mixture of 0.4 g (1.9 mmol) of 6-hydroxy-5-acetylacenaphthene (**VIIe**) and 0.3 ml (6 mmol) of hydrazine hydrate was boiled for 2 h in 3 ml of ethanol with 2 drops of acetic acid. On cooling the separated precipitate was filtered off to obtain 0.2 g (51%) of orange crystals, mp 189–190°C (from acetonitrile) (publ.: mp 191–192°C [16]). IR spectrum, ν, cm^{-1}: 3250, 3200, 3050 (NH), 1620, 1600. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.06 s (3H, 3-Me), 3.23 br.s (4H, CH_2–CH_2), 6.08 d (1H, H^9, $J_{9,8}$ 7.4 Hz), 6.56 d (1H, H^4, $J_{4,5}$ 7.0 Hz), 6.88 d (1H, H^8, $J_{8,9}$ 7.4 Hz), 6.96 d (1H, H^5, $J_{5,4}$ 7.0 Hz), 7.78 br.s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 208 (100) $[M]^{+\cdot}$, 207 (90), 206 (15), 192 (10), 178 (15), 166 (17), 152 (20), 139 (35). Found, %:

C 80.48; H 6.00; N 13.37. $C_{14}H_{12}N_2$. Calculated, %: C 80.76; H 5.76; N 13.46.

1,3-Dimethyl-1*H*-acenaphtho[5,6-*de*]pyridazine (IXf), "1,3-dimethylaceperidazine". A dispersion of 0.5 g (2.3 mmol) of 6-hydroxy-5-acetylacenaphthene (**VIIe**) and 0.15 ml (2.8 mmol) of methylhydrazine was boiled for 7 h in 3 ml of ethanol with 2 drops of acetic acid. The reaction mixture was filtered while hot, and the filtrate was evaporated to dryness. The dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide. After removing chloroform we obtained 0.46 g (87%) of orange crystals, mp 128–129°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.07 s (3H, 3-Me), 3.17 t (2H, 6-CH_2, $J_{6,7}$ 7.0 Hz), 3.27 t (2H, 7-CH_2, $J_{7,6}$ 7.0 Hz), 3.32 s (3H, NMe), 5.92 d (1H, H^9, $J_{9,8}$ 7.5 Hz), 6.90 d (1H, H^4, $J_{4,5}$ 7.1 Hz), 6.95 d.t (1H, H^8, $J_{8,9}$ 7.5, $J_{8,7}$ 1.4 Hz), 6.98 d.t (1H, H^5, $J_{5,4}$ 7.1, $J_{5,6}$ 1.4 Hz). Found, %: C 81.38; H 6.04; N 12.32. $C_{15}H_{14}N_2$. Calculated, %: C 81.08; H 6.31; N 12.61.

1,3-Dimethyl-1*H*-6,7-dehydroacenaphtho[5,6-*de*]-pyridazine (X), "1,3-dimethylaceperidazylene". A dispersion of 0.35 g (1.5 mmol) of 1,3-dimethylaceperidazine (**IXf**) and 0.39 g (1.5 mmol) of chloranil in toluene was boiled for 1 h. The reaction mixture was filtered while hot, and the filtrate was evaporated to dryness. The dry residue was dissolved in chloroform and subjected to column chromatography on aluminum oxide. We obtained 0.3 g (86%) of golden-yellow crystals, mp 158–160°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.87 s (3H, 3-Me), 4.28 s (3H, NMe), 7.15 d (1H, H^9, $J_{9,8}$ 8.1 Hz), 7.63 d (1H, H^6, $J_{6,7}$ 4.1 Hz), 7.78 d (1H, H^4, $J_{4,5}$ 7.5 Hz), 7.80 d (1H, H^7, $J_{7,6}$ 4.1 Hz), 8.37 d (1H, H^8, $J_{8,9}$ 8.1 Hz), 8.48 d (1H, H^5, $J_{5,4}$ 7.5 Hz). Found, %: C 81.50; H 5.23; N 12.98. $C_{15}H_{12}N_2$. Calculated, %: C 81.82; H 5.45; N 12.73.

3-Methyl-9-(3-methyl-1*H*-acenaphtho[5,6-*de*]-pyridazin-1-yl)-1*H*-acenaphtho[5,6-*de*]pyridazine (XI), "3-methyl-9-(3-methylaceperidazin-1-yl)-aceperidazine". To a dispersion of 0.1 g (0.5 mmol) of 3-methylaceperidazine (**IXe**) in 3 ml of ether was added a solution of 0.11 g (0.5 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone in 3 ml of ether, and the mixture was stirred at ~ 20°C for 1 h. The separated precipitate was filtered off and subjected to chromatography on aluminum oxide (eluent ether). We obtained 70 mg (36%) of orange crystals, mp 228–229°C. IR spectrum, ν, cm^{-1}: 3280, 3200, 3050 (NH), 1594, 1575, 1500. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s (3H, 3-Me), 2.20 s (3H, 3'-Me), 3.15 br.s [8H, $(CH_2)_4$], 5.92 d (1H, H^9, $J_{9,8}$ 7.6 Hz), 6.68 d (1H, H^4, $J_{4,5}$ 6.5 Hz), 6.71 d (1H, H^5, $J_{5,4}$ 6.5 Hz), 6.87 d (1H, H^8, $J_{8,9}$ 7.6 Hz), 7.02 d (1H, H$^{4'}$, $J_{4',5'}$ 5.5 Hz), 7.05 d (1H, H$^{5'}$, $J_{5',4'}$ 5.5 Hz), 7.06 s (1H, H^8), 7.85 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 18.30, 18.52, 30.03, 30.18, 31.15, 31.17, 101.66, 114.47, 114.58, 115.83, 120.33, 120.68, 121.12, 121.34, 122.72, 123.56, 124.08, 124.26, 131.27, 132.80, 132.91, 135.82, 139.61, 140.75, 143.52, 143.90, 144.03, 145.15. Mass spectrum, *m/z* (I_{rel}, %): 414 (100) [*M*]$^{+\cdot}$, 413 (75), 399 (40), 383 (28), 373 (10), 356 (10), 207 (35) [*M*]$^{++}$, 206 (25), 193 (20), 177 (33), 164 (22), 151 (35). Found, %: C 81.44; H 4.91; N 13.68. $C_{28}H_{22}N_4$. Calculated, %: C 81.16; H 5.31; N 13.53. *M* 412.28.

3-Methyl-9-(3-methyl-1*H*-acenaphtho[5,6-*de*]pyridazin-1-yl)-1*H*-6,7-dehydroacenaphtho[5,6-*de*]-pyridazine (XII), "3-methyl-9-(3-methylaceperidazin-1-yl)aceperidazylene". To a suspension of 0.2 g (1 mmol) of 3-methylaceperidazine (**IXe**) [16] in 10 ml of ether was added a solution of 0.33 g (1.5 mmol)

Table 2. Some bond angles (φ, deg) in compound **XIIIa**

Angle	φ, deg	Angle	φ, deg
$N^{2A}N^{1A}C^{10A}$	125.5 (3)	$C^{2B}N^{1B}C^{10B}$	124.8 (3)
$C^{1A}N^{2A}N^{1A}$	119.0 (3)	$N^{2B}N^{1B}C^{9A}$	115.4 (3)
$C^{5A}O^{1A}C^{13A}$	116.9 (3)	$C^{10B}N^{1B}C^{9A}$	117.7 (4)
$N^{2A}C^{1A}C^{2A}$	122.6 (4)	$C^{1B}N^{2B}N^{1B}$	118.2 (4)
$N^{2A}C^{1A}C^{12A}$	117.4 (4)	$C^{5B}O^{1B}C^{13B}$	117.0 (4)
$C^{2A}C^{1A}C^{12A}$	120.0 (4)	$N^{2B}C^{1B}C^{2B}$	122.7 (4)
$C^{3A}C^{2A}C^{11A}$	119.7 (3)	$N^{2B}C^{1B}C^{12B}$	116.9 (4)
$C^{3A}C^{2A}C^{1A}$	123.8 (4)	$C^{2B}C^{1B}C^{12B}$	120.3 (4)
$C^{11A}C^{2A}C^{1A}$	116.4 (4)	$C^{3B}C^{2B}C^{11B}$	119.0 (4)
$C^{2A}C^{3A}C^{4A}$	120.5 (4)	$C^{3B}C^{2B}C^{1B}$	123.6 (4)
$C^{5A}C^{4A}C^{3A}$	120.2 (4)	$C^{11B}C^{2B}C^{1B}$	117.4 (3)
$C^{4A}C^{5A}O^{1A}$	124.9 (4)	$C^{2B}C^{3B}C^{4B}$	121.0 (5)
$C^{4A}C^{5A}C^{6A}$	122.1 (3)	$C^{5B}C^{4B}C^{3B}$	120.1 (4)
$O^{1A}C^{5A}C^{6A}$	112.9 (4)	$O^{1B}C^{5B}C^{4B}$	125.3 (4)
$C^{7A}C^{6A}C^{5A}$	124.2 (3)	$O^{1B}C^{5B}C^{6B}$	112.9 (4)
$C^{7A}C^{6A}C^{11A}$	119.2 (4)	$C^{4B}C^{5B}C^{6B}$	121.8 (4)
$C^{5A}C^{6A}C^{11A}$	116.6 (4)	$C^{7B}C^{6B}C^{11B}$	121.2 (4)
$C^{8A}C^{7A}C^{6A}$	120.1 (3)	$C^{7B}C^{6B}C^{5B}$	122.9 (4)
$C^{7A}C^{8A}C^{9A}$	121.5 (4)	$C^{11B}C^{6B}C^{5B}$	115.9 (4)
$C^{10A}C^{9A}C^{8A}$	120.0 (4)	$C^{8A}C^{7B}C^{6B}$	117.8 (4)
$C^{10A}C^{9A}N^{1B}$	119.9 (3)	$C^{9B}C^{8B}C^{7B}$	122.6 (5)
$C^{8A}C^{9A}N^{1B}$	120.0 (4)	$C^{8B}C^{9B}C^{10B}$	120.6 (4)
$C^{9A}C^{10A}N^{1A}$	123.7 (4)	$C^{9B}C^{10B}N^{1B}$	123.9 (4)
$C^{9A}C^{10A}C^{11A}$	120.3 (3)	$C^{9B}C^{10B}C^{11B}$	119.9 (4)
$N^{1A}C^{10A}C^{11A}$	116.0 (4)	$N^{1B}C^{10B}C^{11B}$	116.2 (4)
$C^{10A}C^{11A}C^{6A}$	118.8 (4)	$C^{2B}C^{11B}C^{10B}$	119.9 (4)
$C^{10A}C^{11A}C^{2A}$	120.4 (3)	$C^{2B}C^{11B}C^{6B}$	122.1 (4)
$C^{6A}C^{11A}C^{2A}$	120.7 (3)	$C^{10B}C^{11B}C^{6B}$	117.9 (4)

of 3,5-di-*tert*-butyl-1,2-benzoquinone in 3 ml of ether. In 3–5 min the solid substance dissolved. On evaporating ether the arising dark glassy substance was dissolved in chloroform and subjected to chromatography on aluminum oxide to obtain 0.1 g (51%) of orange crystals, mp 145–147°C. IR spectrum, ν, cm^{-1}: 2890 (NH), 1635, 1620, 1580 (C=N$_{arom}$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.05 s (3H, 3-Me), 2.58 s (3H, 3'-Me), 3.20 t (2H, C^{6}H$_2$, $J_{6,7}$ 7.0 Hz), 3.30 t (2H, C^{7}H$_2$, $J_{7,6}$ 7.0 Hz), 5.84 d (1H, H^9, $J_{9,8}$ 7.6 Hz), 6.68 d (1H, H^4, $J_{4,5}$ 7.1 Hz), 6.74 d.t (1H, H^8, $J_{8,9}$ 7.60, $J_{8,7}$ 1.4 Hz), 7.06 d.t (1H, H^5, $J_{5,4}$ 7.1, $J_{5,6}$ 1.4 Hz), 7.65 d (1H, H$^{6'}$, $J_{6',7'}$ 4.6 Hz), 7.66 d (1H, H$^{4'}$, $J_{4',5'}$ 7.6 Hz), 7.80 d (1H, H$^{7'}$, $J_{7',6'}$ 4.6 Hz), 8.45 s (1H, H$^{8'}$), 8.46 d (1H, H$^{5'}$, $J_{5',4'}$ 7.6 Hz), 10.70 br.s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 413 [M + 1]$^+$ (35), 412 [M]$^+$ (100), 410 [T$_2$] (80), 397 (40), 384 [T$_4$] (80), 382 [T$_3$] (60), 355 (20), 207 [T$_1$] (50), 57 (95), 41 (30). Found, %: C 81.74; H 4.71; N 13.78. $C_{28}H_{20}N_4$. Calculated, %: C 81.56; H 4.85; N 13.58.

A mixture of dimers XI and XII. To a solution of 270 mg (1.3 mmol) of 3-methylaceperidazine (**IXe**) in 5 ml of benzene was added a solution of 480 mg (1.3 mmol) of potassium ferrocyanide $K_3[Fe(CN)_6]$ and 50 mg (1.3 mmol) of sodium hydroxide in 5 ml of water. The emulsion formed was stirred for 2 h. The benzene layer was separated, evaporated, and the powder obtained was subjected to chromatography on aluminum oxide (eluent chloroform). The first fraction contained 180 mg of inseparable mixture of dimers **XI** and **XII** in a ratio ~2:1 (from comparison of intergral intensities in the ^{1}H NMR spectrum).

3-Methyl-9-(3-methyl-6-methoxy-1*H*-naphtho-[1,8-*de*]-pyridazin-1-yl)-6-methoxy-1*H*-naphtho[1,8-*de*]-pyridazine (XIIIa), "3-methyl-9-(3-methyl-6-methoxyperidazin-1-yl)-6-methoxyperidazine". To a suspension of 0.086 g (0.4 mmol) of 3-methyl-6-methoxyperidazine (**VIIa**) in 5 ml of ether was added a solution of 0.089 g (0.42 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone, and the mixture was left standing for 1 h. The separated precipitate was filtered off, dissolved in chloroform and subjected to chromatography on aluminum oxide. Yield 0.025 g (30%), pale yellow powder, mp 175–177°C (from toluene). IR spectrum, ν, cm^{-1}: 1600, 1594, 1580, 1514. ^{1}H NMR spectrum, δ, ppm: 2.15 s (3H, 3'-Me), 2.2 s (3H, 3-Me), 4.0 s [6H, 6,6'-(MeO)$_2$], 6.1 d (1H, H^9, $J_{9,8}$ 7.7 Hz), 6.7–6.78 m (2H, H^7, H$^{7'}$), 6.82–6.9 m (2H, H^5, H$^{5'}$), 7.1 t (1H, H^8, $J_{8,7}$ 8.0, $J_{8,9}$ 8.0 Hz), 7.24–7.34 m (3H, H^4, H$^{4'}$, H$^{8'}$), 8.1 s (1H, NH, disappeared on deuteration). Found, %: C 73.67; H 5.45; N 13.46. $C_{26}H_{22}N_4O_2$. Calculated, %: C 73.93; H 5.21; N 13.27.

Compounds **XIIIb–XIIId** were similarly obtained.

6-Methoxy-9-(6-methoxy-3-ethyl-1*H*-naphtho-[1,8-*de*]pyridazin-1-yl)-3-ethyl-1*H*-naphtho[1,8-*de*]pyridazine (XIIIb), "6-methoxy-9-(6-methoxy-3-ethylperidazin-1-yl)-3-ethylperidazine". Yield 20%, mp 226–228°C (from toluene). IR spectrum, ν, cm^{-1}: 1600, 1596, 1580, 1514 . ^{1}H NMR spectrum, δ, ppm: 1.2 m (6H, 2Me from 3-Et and 3'-Et), 2.6 m (4H, 2CH$_2$ from 3-Et and 3'-Et), 4.0 s [6H, 6,6'-(MeO)$_2$], 6.1 d (1H, H^9, $J_{9,8}$ 7.5 Hz), 6.7–6.8 m (2H, H^7, H$^{7'}$), 6.85–6.95 m (2H, H^5, H$^{5'}$), 7.1 t (1H, H^8, $J_{8,7}$ 7.8, $J_{8,9}$ 7.8 Hz), 7.2–7.35 m (3H, H^4, H$^{4'}$, H$^{8'}$), 8.1 s (1H, NH, disappeared on deuteration). Found, %: C 74.67; H 5.43; N 12.66. $C_{28}H_{26}N_4O_2$. Calculated, %: C 74.66; H 5.77; N 12.44.

6-Methoxy-9-(6-methoxy-3-phenyl-1*H*-naphtho-[1,8-*de*]pyridazin-1-yl)-3-phenyl-1*H*-naphtho[1,8-*de*]pyridazine (XIIIβ), "6-methoxy-9-(6-methoxy-3-phenylperidazin-1-yl)-3-phenylperidazine". Yield 32%, mp 207–209°C (from toluene). IR spectrum, ν, cm^{-1}: 1590, 1580, 1515 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 4.0 s [6H, 6,6'-(MeO)$_2$], 6.2 d (1H, H^9, $J_{9,8}$ 7.8 Hz), 6.6–7.8 m (18H, H$_{arom}$), 8.4 s (1H, NH, disappeared on deuteration). Found, %: C 78.87; H 5.03; N 10.60. $C_{36}H_{26}N_4O_2$. Calculated, %: C 79.12; H 4.76; N 10.25.

3-(4-Morpholino)-9-{(4-morpholino)-1*H*-naphtho[*de*]pyridazin-1-yl}-1*H*-naphtho[*de*]-pyridazine (XIIIe), "3-(4-morpholino)-9-[(4-morpholino)peridazin-1-yl]peridazine". Yield 27%, mp 273–275°C (from toluene). IR spectrum, ν, cm^{-1}: 3380, 1607, 1570, 1515. ^{1}H NMR spectrum, δ, ppm: 3.1 br.s [8H, 3,3'-(NCH$_2$)$_4$], 3.9 br.s [8H, 3,3'-(OCH$_2$)$_4$], 6.0–7.7 m (11H, H$_{arom}$), 8.3 br.s (1H, NH, disappeared on deuteration). Found, %: C 71.80; H 5.33; N 16.40. $C_{30}H_{28}N_6O_2$. Calculated, %: C 71.42; H 5.55; N 16.66.

REFERENCES

1. Lacy, P.H. and Smith, D.C.C., *J. Chem. Soc. C,* 1971, p. 747.
2. Pozharskii, A.F. and Dal'nikovskaya, V.V., *Usp. Khim*., 1981, vol. 50, p. 1559.
3. Pozharskii, A.F., Vinokurova, T.I., and Zaletov, V.G., *Khim. Geterotsikl. Soedin.,* 1976, p. 539.
4. Vinokurova, T.I. and Pozharskii, A.F., *Khim. Geterotsikl. Soedin.,* 1976, p. 545.
5. Shelepin, O.E., *Khimiya peritsiklicheskikh soedinenii* (Chemistry of Pericyclic Compounds), Rostov-on-Don: Izd. RGU, 1973, p. 240.
6. Boekelheide, V. and Vick, G.K., *J. Am. Chem. Soc.,* 1956, vol. 78, p. 653.

7. Gerson, F., Heilbronner, E., and Boekelheide, V., *Helv. Shim. Acta,* 1964, vol. 47, p. 1172.
8. Gardner, P.D. and Thomson, R.G., *J. Org. Chem.,* 1957, vol. 22, p. 36.
9. Pozharskii, A.F., *Teoreticheskie osnovy khimii geterotsiklov* (Theoretical Bases of Chemistry of Heterocycles), Moskva: Khimiya, 1985, p. 280.
10. Kashparov, I.S. and Pozharskii, A.F., *Khim. Geterotsikl. Soedin.,* 1985, p. 372.
11. Mezheritskii, V.V., *Nauchnaya mysl' Kavkaza* (Scientific Thought of the Caucasus), Zhdanov, Yu.A., Ed., Rostov-on-Don: Izd. SKNTs VSh, 2001, p. 46.
12. Mezheritskii, V.V., *Azotistye geterotsikly i alkaloidy* (Nitrogen Heterocycles and Alkaloids), Kartsev, V.G. and Tolstikov, G.A., Moscow: Iridium-Press, 2001, vol. 1, p. 111.
13. Elisevich, D.M., *Cand. Sci. (Chem.) Dissertation*, Rostov-on-Don, 1982.
14. Morkovnik, A.S., Panov, V.B., Elisevich, D.M., and Mezheritskii, V.V., *Zh. Org. Khim.,* 1983, vol. 19, p. 1984.
15. Mezheritskii, V.V., Tkachenko, V.V., Zhukovskaya, O.N., Elisevich, D.M., and Dorofeenko, G.N., *Zh. Org. Khim.,* 1981, vol. 17, p. 627.
16. Bystritskii, G.I., Vorozhtsov, G.N., Dokunikhin, N.S., and Ovsyannikova, S.V., *Zh. Org. Khim.,* 1973, vol. 9, p. 1067.
17. Mezheritskii, V.V., Pikus, A.L., Spasov, A.A., Ostrovskii, O.V., Dudchenko, G.P., and Kosolapov, V.A., *Khim. Fiz. Zh*., 1998, p. 15.
18. Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.J., and Taylor, R., *J. Chem. Soc., Perkin Trans. 2*, 1987, p. 1.
19. Elisevich, D.M., Mezheritskii, V.V., Panov, V.B., and Kazakov, A.L., *Zh. Org. Khim.,* 1984, vol. 20, p. 1474.
20. Dmitriev, A.B., Okolelova, M.S., Bogdashev, N.N., Elisevich, D.M., and Kazakov, A.L., *Khim. Geterotsikl. Soedin.,* 1987, p. 1098.
21. Strel'tsov, V.A. and Zavodnik, V.E., *Kristallografiya*, 1989, vol. 34, p. 1369.
22. Sheldrick, G.M., *SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data, Rev. 5.02*., Seimens Analytical X-ray Instruments, Inc., Germany, 1994.