Reactions of 1-Nitrocyclohexene with *N***,***N***-Binucleophiles**

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Received February 25, 2010

Abstract—A modification of 1-nitrocyclohexene synthesis is proposed; its reaction with phenylhydrazine and benzoic acid hydrazide is shown to afford monoadducts, and with hydrazine hydrate, bisaduct. With diphenylguanidine occurs heterocyclization to 1-phenyl-2-*N*-phenylamino-4,5,6,7-tetrahydrobenzimidazole, whose structure is confirmed by the X-ray diffraction data. The analysis performed for this compound of the electron density distribution function in the crystal made it possible to estimate the charge distribution, π -electrons delocalization nature, and the role of N–H···N, C–H···H–C and C–H···C interactions in the formation of the crystal packing.

DOI: 10.1134/S1070363210110113

In the chemistry of nitro compounds, which are successfully utilized as the active building blocks in the purposeful synthesis of practically important substances, cyclic conjugated nitroalkenes occupy a significant place. They are used as effective substrates for the addition reactions in designing polynuclear framework systems [1]. In particular, precursors of biologically active alkaloids [2, 3] and compounds possessing cytotoxic activity [4] have been obtained on the basis of 1-nitrocyclohexene.

At the same time the known approaches to the synthesis of 1-nitrocyclohexene [5, 6] have some drawbacks in the practical realization. The nitromercuration method [5] requires the use of mercuric chloride, and the one-pot nitroiodination-dehydrogenation method [6] recommended for synthesis of the wide variety of nitroalkenes is not reproduced in the case of 1-nitrocyclohexene. We have showed that the reaction of sodium nitrite and iodine with cyclohexene under the conditions [6] affords nitroalkene in trace amount. The main product is 2-iodo-1-nitrocyclohexane I (53%) isolated as 2:1 diastereomeric mixture. The target nitroalkene II was obtained by dehydrohalogenation of this diastereomeric mixture with triethylamine in diethyl ether solution in 37% yield.

It should be noted that under these conditions the major diastereomer Ia showed greater ability to HI

elimination to form product **II** quantitatively, whereas the content of minor diastereomer **Ib** in the reaction mixture remained practically unchanged.

The spectral characteristics of the obtained nitroalkene **II** correspond to the published data [7, 8]. In the ¹H NMR spectrum of this compound the signal of olefin proton at 7.27 ppm is present along with the signals of the methylene protons of the ring. The IR spectrum contains absorption bands of C=C bond (1635 cm⁻¹) and the vibrations of the conjugated nitrogroup (1516, 1343, 1334 cm⁻¹).

We studied reaction of 1-nitrocyclohexene II with a series of N,N-binucleophiles, the hydrazine derivatives (phenylhydrazine, benzoic acid hydrazide, and hydrazine hydrate) and diphenylguanidine. The examined nitroalkene II was found to be easily adding these hydrazine derivatives at room temperature in ethanol. In the case of phenylhydrazine and benzoic acid hydrazide the classic Michael adducts formed, 1-nitro-2-hydrazinocyclohexanes III (47%) and IV (78%). The reaction with hydrazine hydrate resulted in the bisaddition product, 1,2-bis(2-nitrocyclohexyl)hydrazine as a mixture of diastereomers Va and Vb (21%).

As a result of the reaction of 1-nitrocyclohexene II with N,N-diphenylguanidine carried out under similar conditions the high-melting crystalline product was isolated. According to the spectral data, 1- phenyl-2-N-



phenylamino-4,5,6,7-tetrahydrobenzimidazole **VI** formed in 24% yield. Taking into account the possibility of the transformations of the 2-substituted nitrocyclohexanes according to the Nef reaction [9, 10], it is logical to assume that this interaction occurs via a series of the consecutive reactions, which include nucleophilic addition of diphenylguanidine at the multiple bond, transformation of nitromethine fragment into the carbonyl initiated by the action of basic reagent, and the subsequent heterocyclization according to Ad_N –Escheme with the participation of ketone and aniline groups.

The structure of obtained compounds I, III-VI was established using IR, ¹H NMR spectroscopy and X-ray diffraction analysis. The ¹H NMR spectra of the 2substituted nitrocyclohexanes I, III-V are similar in the character of the signals of the cyclohexane ring protons. In particular, the vicinal constant values of the methine protons $[{}^{3}J(C^{1}HC^{2}H) 4.20-5.45 \text{ Hz}]$ indicate the axial-equatorial orientation of the ring substituents [11]. Unlike the stereohomogeneous compounds III and IV, the spectra of the products Ia, Ib, Va, and Vb contain the double set of signals, which testify to the existence of these substances as mixtures of erythroand threo-diastereomers. The absence of the signals of NH₂-group protons is characteristic of the ¹H NMR spectrum of the bis-adducts Va and Vb, that along with the elemental analysis data confirm the structure assigned to them.

The IR spectra of compounds I, III–V contain the absorption bands of the non-conjugated nitro-group (1545–1559, 1370–1371 cm⁻¹). The presence of NH-groups absorption (3250-3333 cm⁻¹) is characteristic

of the hydrazine derivatives III–V. In the spectrum of compound IV the absorption band at 1627 cm^{-1} originated from the conjugated carbonyl group.

The ¹H NMR spectrum of the fused heterocyclic structure **VI** contains multiplets of methylene protons of the cyclohexene fragment (1.70, 2.27 ppm), phenyl protons (6.65, 7.03, 7.48 ppm), and also a singlet signal of NH-proton (7.76 ppm). In the IR spectra of adduct **VI** there are the absorption bands of C=C and C=N bonds (1595, 1617 cm⁻¹) and of NH-group (3340 cm⁻¹).

The unequivocal confirmation of 1-phenyl-2-*N*-phenylamino-4,5,6,7-tetrahydrobenzimidazole **VI** structure were obtained by the data of X-ray diffraction analysis shown in Figs. 1–3 and in Tables 1 and 2; the atoms numeration corresponds to that in Fig. 1. The imidazole ring of the molecule is planar with an insignificant deviation of the C⁴ atom; the planes of phenyl ring and aniline fragment are turned relative to the heterocycle to the different sides (torsion angles $C^1N^2C^{17}C^{18}$ and $N^2C^1N^{10}C^{11}$ are 53.79 and –56.97°, respectively).

The high quality of the studied crystals made it possible to obtain the high-angle data array which made it possible to analyze the electron density distribution $\rho(\mathbf{r})$ in the crystal. The deformation electron density distribution (DED) in the imidazole ring is close to that expected: the DED maxima are localized in the region of chemical bonds and lone electron pairs of the atoms N⁵ and N¹⁰. On the basis of the topological analysis of $\rho(\mathbf{r})$ within Bader's "Atoms in Molecules" theory [12, 13] we obtained atomic charges [by integration of $\rho(\mathbf{r})$ over the atomic basin], localized critical points (3, -1) (chemical bonds



Fig. 1. (a) General view of compound **VI** in the representation of atoms by thermal ellipsoids (p 50%). (b) Distribution of deformation electron density in the imidazole ring plane. Isolines are drawn with the step 0.1 e Å⁻³, negative values are shown by dotted line.

indicators) and determined the bond ellipticities (ε) values (the values which reproduce the bond multiplicity). The analysis of nuclear charges showed that the negative charge in the heterocycle is predominantly localized on the nitrogen atoms (N² and N⁵ atomic charges are equal to -0.96 and -0.85 *e* respectively),

and maximum positive charge (+0.96 *e*) is on the carbon atom C¹. Atomic charges of C³ and C⁴ are substantially lower and equal 0.05 and 0.27 *e*, respectively. The values ε in the imidazole ring indicate the considerable electron delocalization with the minimum value ε 0.12 on the bond N⁵–C⁴ and



Fig. 2. Centrosymmetrical dimers bonded due to (a) N-H…N and (b) C-H…H-C contacts.



Fig. 3. The vectorial field of the electron density gradient of (thin lines), and also bonding ways (thick lines) and interatomic surfaces (line of average width) in the region of H…H interactions.

Bond	l, Å	Bond	l, Å
C^1-N^5	1.3214(4)	N ² -C ¹⁷	1.4274(4)
C^1-N^2	1.3762(4)	C^3-C^4	1.3607(5)
$C^1 - N^{10}$	1.3806(4)	C^4-N^5	1.3938(4)
$N^2 - C^3$	1.4000(4)	N ¹⁰ -C ¹¹	1.4100(4)
Angle	deg	Angle	deg
$N^5C^1N^2$	111.93(3)	$N^2C^3C^6$	127.48(3)
$N^{5}C^{1}N^{10}$	125.72(3)	$C^{3}C^{4}N^{5}$	110.76(3)
$N^{2}C^{1}N^{10}$	122.26(3)	$C^{3}C^{4}C^{9}$	123.35(3)
$C^1 N^2 C^3$	106.34(3)	$N^5C^4C^9$	125.86(3)
$C^{1}N^{2}C^{17}$	125.99(3)	$C^1N^5C^4$	105.16(3)
$C^{3}N^{2}C^{17}$	126.50(3)	$C^{1}N^{10}C^{11}$	121.69(3)
$C^4 C^3 N^2$	105.76(3)	$C^{1}N^{10}H^{10N}$	111.9(6)
$C^4C^3C^6$	126.75(3)	$C^{11}N^{10}H^{10N}$	116.7(7)

Table 1. Bond lengths (Å) and valence angles (deg) for compound VI

 Table 2. Main crystallographic data and refinement parameters for compound VI

$C^1N^2C^3$	106.34(3)	$N^5C^4C^9$	125.86(3)	b, A
$C^{1}N^{2}C^{17}$	125.99(3)	$C^1N^5C^4$	105.16(3)	<i>c</i> , Å
$C^{3}N^{2}C^{17}$	126.50(3)	$C^1 N^{10} C^{11}$	121.69(3)	α, °
$C^4 C^3 N^2$	105.76(3)	$C^{1}N^{10}H^{10N}$	111.9(6)	β, °
$C^4C^3C^6$	126.75(3)	$C^{11}N^{10}H^{10N}$	116.7(7)	γ. °
				V, Å ³
maximum on	$d_{\rm calc}$, g cm ⁻³			
the value ε for	μ , cm ⁻¹			
spite of consi	<i>F</i> (000)			
(sum of bond	$2\theta_{max}$, deg			
values of ε fo	Number of n			
to 0.21 and 0.	Number of in			
The searc	Number of re			
intermolecula	in interactions	showed that	beside the	Number of r

intermolecu strong hydrogen bond [N¹⁰...N^{5A} 2.918(1) Å. N¹⁰H¹⁰N^{5A} 174°] (Fig. 2) joining molecules into the dimers, a series of weak interactions C-H $\cdots\pi$, C-H \cdots N and H.H. can be identified. All the contacts indicated, including the N-H···N hydrogen bond, belong to interactions of the closed shells, as indicated by the positive value of the local density of electron energy at the appropriate critical points (3, -1). In order to evaluate the energy of intermolecular interactions and of crystalline packing we used the approach we formerly had developed [14-16] based on the correlation dependence of interaction energy on the potential energy density at critical point (3, -1) [17]. The summing up of the energy of all independent contacts led to the crystalline packing energy equal 21.1 kcal mol^{-1} .

As would be expected, the main contribution (35%) to the formation of crystalline packing originates from the hydrogen bond $N^{10}-H^{10N}\cdots N^{5A}$, whose energy is 7.5 kcal mol⁻¹. For evaluating the accuracy of this value we performed the calculation (PBE1PBE/6-311G**) of the isolated molecule and hydrogen-

Parameter	Value		
Formula	$C_{19}H_{19}N_3$		
Molecular mass	289.37		
Т, К	100		
Crystal system	Triclinic		
Space group	<i>P</i> -1		
Ζ	2		
<i>a</i> , Å	8.5649(2)		
<i>b</i> , Å	9.2728(2)		
<i>c</i> , Å	9.9162(2)		
α, °	80.9133(8)		
β, °	85.8953(8)		
γ, °	72.6459(8)		
V, Å ³	742.02(3)		
$d_{\rm calc}$, g cm ⁻³	1.295		
μ , cm ⁻¹	0.78		
<i>F</i> (000)	308		
$2\theta_{max}$, deg	110		
Number of measured reflections	118613		
Number of independent reflections	18658		
Number of reflections with $I > 2\sigma(I)$	13575		
Number of refined parameters	275		
<i>R</i> 1	0.0406		
wR2	0.1318		
GOF	1.084		
Residual electron density, e Å ⁻³ (d_{\min}/d_{\max})	0.419/-0.290		
Multipole refinement			
Number of reflections with $I > 3\sigma(I)$	3308		
R1, calculated by F	0.0223		
<i>Rw</i> , calculated by <i>F</i>	0.0231		
GOF	0.8358		
Residual electron density, e Å ⁻³ (d_{\min}/d_{\max})	0.15/-0.192		

bonded dimer. During the dimer optimization the parameters of hydrogen bond did not actually change, in particular, the distance $N^{5A} \dots N^{10}$ is 2.957 Å. The dimerization energy for this H-bonded dimer is 15.53 kcal mol⁻¹, i.e., 7.76 kcal mol⁻¹ to one hydrogen bond. Thus, it is possible to see that the energy of hydrogen bond in the crystal obtained by us from X-ray diffraction data is evaluated with the sufficiently high accuracy.

Besides the H-bonded dimer, in this crystal also exists the centrosymmetrical dimer formed due to sufficiently unusual directed interactions C-H···H-C $(H^{12} \cdots H^{13A} 2.34 \text{ Å}, C^{12}H^{12}H^{13A} 178^{\circ}, H^{12}H^{13A}C^{13A} 61^{\circ})$ (Fig. 2b). The search for critical points showed that, although hydrogen atoms bear identical positive charge, these contacts correspond to bonding interactions. Moreover, critical point (3, -1) was also localized for interaction between the hydrogen atoms H¹² (H···H 2.36 Å, C¹²H¹²H^{12A} 117°), connected with the inversion center, and also for the contact C-H··· π (H¹³...C^{3A} 2.92 Å, C¹³H¹³C^{3A} 139°). (Fig. 2b). The energy of H...H interactions proves to be even higher than $H \cdots C$ (0.7 kcal mol⁻¹) and equals ~1 kcal mol⁻¹. In this case the total energy of CH---CH-bonded dimer reaches 2 kcal mol⁻¹. Thus, it is possible to conclude that, although the hydrogen bond N-H…N is the most strong in the crystal, the main contribution to the crystal lattice energy (75%) is provided by the weak interactions H···H and H···C. Therefore the directed design of crystalline materials for the compounds with a low number of functional groups capable to form stable supramolecular synthons, is complex and today actually insoluble problem.

Thus, as a result of this study a modification of the synthesis method of 1-nitrocyclohexene is developed. It is shown that the reaction of the latter with hydrazine derivatives affords the products of mono- or bisaddition, while the reaction with the diphenylguanidine vields a binuclear system containing fused cyclohexene and imidazole rings, 1-phenyl-2-N-penylamino-4,5,6,7-tetrahydrobenzimidazole. We per-formed analysis of the function of the electron density distribution for this compound in the crystal by the method of X-ray diffraction that allowed to estimate the charge distribution, the nature of p-electrons delocalization, and the role of interactions N-H...N, C-H···H-C and C-H···C in the crystalline packing formation.

EXPERIMENTAL

The ¹H, ¹³C, HMQC NMR spectra were registered on a Jeol ECX400A spectrometer at operating frequencies 100.52 (¹³C) and 399.78 (¹H) MHz, respectively, in DMSO- d_6 using the signals of the residual protonated solvent as reference signals. The IR spectrum was taken on a Shimadzu IR-21 Prestige Fourier-spectrometer from KBr. The elemental analysis was performed on a Eurovector EA3028 analyzer. The reaction progress was monitored by TLC on Silufol UV-254 plates with detecting on a chromatoscope.

X-Ray diffraction analysis of compound VI was performed on a SMART APEX II CCD diffractometer (Mo K_{α} radiation, graphite monochromator, ω scanning). The structure was solved by the direct method and refined by means of full-matrix leastsquares procedure on F_{hkl}^2 in anisotropic approximation. In the structure VI the hydrogen atoms were localized from differential Fourier charts and refined in isotopic approximation. The main crystallographic data for structure VI are given in Table 2. All calculations were performed using WinGX program package [4]. Figure was made by means of SHELXTL PLUS program [18].

Multipole refinement for the structure VI was performed within Hansen-Koppens's formalism [19] using XD program package [20] with the core and valence electron density obtained from the wave functions based on the relativistic solution of the Dirac-Fock equation. Before refining the C-H and N-H bond lengths were normalized to standart values 1.08 Å, and 1.03 Å, respectively. Multipole expansions for oxygen, nitrogen and carbon atoms were limited to octupole level, for hydrogen atoms, to dipole one. In the case of hydrogen atom of NH-group we refined the occupation of hexadecapole H₄₀ for the more correct description of hydrogen bonds. The refinement was made by F_{hkl} . All covalently bound atom pairs satisfied the Hirschfeld's criterion on the bond rigidity [21]. The residual electron density did not exceed 0.15 e $Å^{-3}$. For calculation of $v(\mathbf{r})$ from the X-ray diffraction data we used approximation within Thomas–Fermi theory [22]. By this approach, the kinetic energy density $g(\mathbf{r})$ can be taken from the equation: $g(\mathbf{r}) = 3/10(3\pi^2)^{2/3} [\rho(\mathbf{r})]^{5/3} +$ $(1/72)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r}) + 1/6\nabla^2\rho(\mathbf{r})$ in combination with the local virial theorem [22]: $2g(\mathbf{r}) + v(\mathbf{r}) = 1/4\nabla^2 \rho(\mathbf{r})$, which provides a possibility to calculate both the potential energy and local energy densities $h_e(\mathbf{r})$. The search for critical points (3, -1) and calculating topological characteristics $\rho(\mathbf{r})$, including $h_e(\mathbf{r})$, $g(\mathbf{r})$ and $v(\mathbf{r})$, was performed with use of WINXPRO program [23].

Quantum-chemical calculations were made with the Gaussian 03 package [24]. The standard values of maximal force and mean-square shifting 4.5×10^{-4} and 1.8×10^{-3} au, respectively, were used as convergence criteria. Topological analysis of the wave function was carried out using AIMAll program package [25].

1-Nitro-2-iodocyclohexane (Ia, Ib) (diastereomeric mixture, a:b = 2:1). To a solution of 13.24 g (196 mmol) of sodium nitrite and 8.05 ml (144 mmol) of ethylene glycol in 20 ml of water was added a solution of 4.86 ml (48 mmol) of cyclohexene in 150 ml of ethyl acetate. The mixture was cooled to 0°C, then 18.3 g (72 mmol) of iodine was added. The reaction mixture was stirred at room temperature for 96 h under nitrogen. The organic layer was separated, washed with saturated solution of sodium thiosulfate, dried over anhydrous magnesium sulfate, and concentrated in a reduced pressure. Yield 6.49 g (53%), yellow oil, bp 110–112°C (3 mm Hg). IR spectrum, v, cm^{-1} (CHCl₃): 1557, 1370 (NO₂). ¹H NMR spectrum (DMSO- d_6), δ , ppm: diastereomer Ia, 1.38 m (2H, $C^{5}H_{2}$, 1.95 m (2H, $C^{4}H_{2}$), 2.31 m (2H, $C^{3}H_{2}$), 2.53 m (2H, C⁶H₂), 4.40 d.d.d [1H, C²H, ³*J*(C¹HC²H) 4.28, ${}^{3}J(C^{2}HC^{3}H_{A})$ 10.36, ${}^{3}J(C^{2}HC^{3}H_{B})$ 7.60 Hz], 4.62 d.t [1H, $C^{1}H, {}^{3}J(C^{1}HC^{2}H) 4.28, {}^{3}J(C^{1}HC^{6}H_{A}) = {}^{3}J(C^{1}HC^{6}H_{B})$ 10.70 Hz]; diastereomer **Ib**: 1.38 m (2H, $C^{5}H_{2}$), 1.95 m $(2H, C^{4}H_{2}), 2.42 \text{ m} (2H, C^{3}H_{2}), 2.46 \text{ m} (2H, C^{6}H_{2}),$ 3.63 d.t [1H, C²H, ${}^{3}J(C^{1}HC^{2}H)$ 4.28, ${}^{3}J(C^{2}HC^{3}H_{A}) =$ ${}^{3}J(C^{2}HC^{3}H_{B})$ 10.00 Hz], 4.02 d.d.d [1H, C¹H, ${}^{3}J(C^{1}HC^{2}H)$ 4.28, ${}^{3}J(C^{1}HC^{6}H_{A})$ 9.40, ${}^{3}J(C^{1}HC^{6}H_{B})$ 7.85 Hz]. Mass spectrum, $[M]^+(m/z)$: 255.

1-Nitrocyclohexene (II). To a solution of 5 g (19.6 mmol) of 2-iodo-1-nitrocyclohexane I in 35 ml of diethyl ether was added a solution of 2.46 ml (17.6 mmol) of triethylamine in 15 ml of diethyl ether. The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was washed with water to pH 7, dried over anhydrous magnesium sulfate, and concentrated in a reduced pressure. The residue was purified by flash chromatography (eluent–hexane). Yield 0.92 g (37%), R_f 0.69. IR spectrum, v, cm⁻¹ (CHCl₃): 1334, 1516 (NO₂), 1635 (C=C). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.55 m (2H, C⁴H₂), 1.70 m (2H, C⁵H₂), 2.30 m (2H, C³H₂), 2.47 m (2H, C⁶H₂), 7.27 m (1H, C²H).

1-Nitro-2-phenylhydrazinocyclohexane (III). To 0.63 g (5 mmol) of 1-nitrocyclohexene **II** was added a solution of 1.1 g (10 mmol) of phenylhydrazine in 2 ml of ethanol–water mixture (1:1). The reaction mixture was kept for 24 h at room temperature. The precipitate was filtered off and dried in air. Yield 0.55 g (47%), mp 109–111C (decomp., ethanol) (115C [26]). IR spectrum, v, cm⁻¹ (KBr): 1546, 1375 (NO₂), 1605 (C=C), 3333 (NH). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 1.25 m (4H, C⁴H₂, C⁵H₂), 1.70 m (2H, C³H₂), 2.15 m (2H, C⁶H₂), 3.05 d.d.d.d [1H, C²H, ³*J*(C¹HC²H)

4.40, ${}^{3}J(C^{2}HC^{3}H_{A}) 8.90$, ${}^{3}J(C^{2}HC^{3}H_{B}) 8.17$, ${}^{3}J(C^{2}HNH) 6.50$ Hz], 4.38 d.d [1H, NH, ${}^{3}J_{NHN'H} 2.00$, ${}^{3}J(C^{2}HNH) 6.50$ Hz], 4.45 d.d.d [1H, C¹H, ${}^{3}J(C^{1}HC^{2}H) 4.40$, ${}^{3}J(C^{1}HC^{6}H_{A}) 11.30$, ${}^{3}J(C^{1}HC^{6}H_{B}) 9.98$ Hz], 6.71 d (1H, N'H, ${}^{3}J_{NHN'H} 2.00$ Hz), 6.51, 6.65, 6.98 m (5H, C₆H₅). Found, %: C 61.56; H 7.41; N 17.89. C₁₂H₁₆N₃O₂. Calculated, %: C 61.26; H 7.28; N 17.86.

1-Nitro-2-(N'-benzoylhydrazino)cyclohexane (IV). To 1 g (8 mmol) of 1-nitrocyclohexene II was added the boiling solution of 1.09 g (8 mmol) of benzoic acid hydrazide in 21 ml of ethanol-water mixture (2:1). The reaction mixture was cooled to room temperature, kept for 24 h, and concentrated on a Petri dish. The precipitate was filtered off, washed with ethanol, and dried in air. Yield 1.64 g (78%), mp 132-135°C (ethanol-water, 1:1). IR spectrum, v, cm^{-1} (KBr): 1559, 1381 (NO₂), 1607 (C=C), 1627 (C=O), 3312 (NH). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.63 m (4H, C⁴H₂, C⁵H₂), 1.68 m (2H, C³H₂), 2.14 m (2H, $C^{6}H_{2}$), 3.33 m (1H, $C^{2}H$), 4.58 m (1H, $C^{1}H$), 5.30 m (1H, NH), 7.40–7.74 m (5H, Ph), 9.86 м (1H, N'H). Found, %: N 16.29. C₁₃H₁₇N₃O₃. Calculated, %: N 15.97.

1,2-Bis(2-nitrocyclohexyl)hydrazine (Va, Vb). To 1 g (8 mmol) of 1-nitrocyclohexene II was added the boiling solution of 0.78 ml (16 mmol) of hydrazine hydrate in 14 ml of ethanol-water mixture (1:1). The reaction mixture was cooled to room temperature, kept for 48 h, the precipitate was filtered off, and dried in air. Yield 0.21 g (21%) (diastereomers mixture, a:b =1:1), mp 102–104°C (ethanol). IR spectrum, v, cm⁻¹ (KBr): 1545, 1379 (NO₂), 3250 (NH). ¹H NMR spectrum (DMSO- d_6), δ , ppm: diastereomer Va, 1.00– 1.30 m (8H, $2C^{4}H_{2}$, $2C^{5}H_{2}$), 1.50-2.10 m (8H, $2C^{3}H_{2}$, $2C^{6}H_{2}$), 2.83 d.d.t [2H, $2C^{2}H$, ${}^{3}J(C^{1}HC^{2}H)$ 5.11, ${}^{3}J(C^{2}HC^{3}H_{2})$ 9.54, ${}^{3}J(C^{2}HNH)$ 5.76 Hz], 3.84 d [2H, 2NH, ${}^{3}J(C^{2}HNH)$ 5.76 Hz), 4.37 d.t [2H, 2C¹H, ${}^{3}J(C^{1}HC^{2}H)$ 5.11, ${}^{3}J(C^{1}HC^{6}H_{2})$ 13.87 Hz]; diastereomer **Vb**: 1.00–1.30 m (8H, $2C^{4}H_{2}$, $2C^{5}H_{2}$), 1.50–2.10 m $(8H, 2C^{3}H_{2}, 2C^{6}H_{2}), 2.79 \text{ d.d.t} [2H, 2C^{2}H, {}^{3}J(C^{1}HC^{2}H)]$ 5.45, ${}^{3}J(C^{2}HC^{3}H_{2})$ 9.13, ${}^{3}J(C^{2}HNH)$ 6.64 Hz], 3.82 d [2H, 2NH, ³*J*(C²HNH) 6.64 Hz], 4.33 d.t [2H, 2C¹H, ${}^{3}J(C^{1}HC^{2}H)$ 5.45, ${}^{3}J(C^{1}HC^{6}H_{2})$ 13.14 Hz]. Found, %: C 50.31; H 7.53; N 19.38. C₁₂H₂₂N₄O₄. Calculated, %: C 50.34; H 7.74; N 19.57.

1-Phenyl-2-phenylamino-4,5,6,7-tetrahydrobenzimidazole (VI). To 1.12 g (8.8 mmol) of 1-nitrocyclohexene II was added the boiling solution of 1.86 g (8.8 mmol) of N,N'-diphenylguanidine in 28 ml of ethanol–water mixture (1:1). The reaction mixture was cooled to room temperature and kept for 24 h. The precipitate was filtered off and dried in air. Yield 0.71 g (24%), mp 204–206°C (benzene). IR spectrum, v, cm⁻¹ (KBr): 1595 (C=C), 1617 (C=N), 3340 (NH). ¹H NMR spectrum (DMSO- d_6), δ , ppm: 1.70 m (6H, C⁴H₂, C⁵H₂, C⁶H₂), 2.27 m (2H, C⁷H₂), 6.65 m, 7.03–7.48 m (10H, Ph), 7.76 s (1H, NH). Found, %: C 79.08; H 6.67; N 14.52. C₁₉H₁₉N₃. Calculated, %: C 78.86; H 6.62; N 14.52.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 10-03-00578-a) and by the President of Russian Federation (grant no. MD-237.2010.3).

REFERENCES

- Perekalin, V.V., Lipina, E.S., Berestovitskaya, V.M., and Efremov, D.A. *Nitroalkenes. Conjugated Nitrocompounds*, Willey, 1994, p. 256.
- Hoshino, O., Ishizaki, M., Saito, K., and Jumoto, K., J. Chem. Soc., Chem. Commun., 1990, vol. 5, p. 420.
- Bartoli, G., Bosco, M., Giuli, S., Guiliani, A., Lucarelli, L., Marcantoni, E., Sambri, L., and Torregiani, E., *J. Org. Chem.*, 2005, vol. 70, no. 5, p. 1941.
- Patra, R., Maiti, S.B., and Chatterjee, A., *Tetrahedron Lett.*, 1991, vol. 32, no. 10, p. 1363.
- Corey, E.J. and Estreicher, H., J. Am. Chem. Soc., 1978, vol. 100, no. 19, p. 6294.
- Sang-sup, Jew, Hee-doo, Kim, Youn-sang, Cho, and Chae-ho, Cook, *Chem. Lett.*, 1986, vol. 15, no. 10, p. 1747.
- Griswold, A.A. and Starcher, P.S., J. Chem. Soc., 1966, vol. 31, p. 357.
- Kunai, A., Yanagi, Y., and Sasaki, K., *Tetrahedron Lett.*, 1983, vol. 24, no. 41, p. 4443.
- 9. Seebach, D. and Golinsky, J., *Helv. Chim. Acta*, 1981, vol. 64, no. 5, p. 1413.
- 10. Vankar, Y.D., Shah, K., Bawa, A., and Singh, S.P., *Tetrahedron*, 1991, vol. 47, no. 42, p. 8883.
- 11. Hunter, H., Vvedenie v kurs spektroskopii YaMR (Introduction to a Course on NMR Spectroscopy), Moscow: Mir, 1984.
- 12. Bader, R.F.W. *Atoms in molecules. A Quantum Theory*, Oxford: Clarendron Press, 1990.
- 13. Bushmarinov, I.S., Lyssenko, K.A., and Antipin, M.Yu., *Usp. Khim.*, 2009, vol. 78, p. 307.

- 14. Lyssenko, K.A., Korlyukov, A.A., and Antipin M.Yu., Mendeleev. Commun., 2005, p. 90.
- Lyssenko, K.A., Korlyukov, A.A., Golovanov, D.G., Ketkov, S.Yu., and Antipin, M.Yu., *J. Phys. Chem. A*, 2006, vol. 110, p. 6545.
- Lyssenko, K.A., Barzilovich, P.Yu., Nelyubina, Yu.V., Astafiev, E.A., Antipin, M.Yu., and Aldoshin, S.M., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2009, no. 1, p. 31.
- 17. Espinosa, E., Alkorta, I., Rozas, I., Elguero, J., and Molins, E., *Chem. Phys. Letts.*, 2001, vol. 336, p. 457.
- Sheldrick, G.M. SHELXTL v. 5.10, Structure Determination Software Suit, Bruker AXS: Madison, Wisconsin, USA.
- 19. Hansen, N.K. and Koppens, P., *Acta Crystallogr. A*, 1978, vol. 34, p. 909.
- Koritsansky, T.S., Howard, S.T., Richter, T., Macchi, P., Volkov, A., Gatti, C., Mallinson, P.R., Farrugia, L.J., Su, Z., and Hansen, N.K., XD-A Computer Program Package for Multipole Refinement and Topological Analysis of Charge Densities from Diffraction Data, 2003.
- 21. Hirshfeld, F.L., Acta. Crystallogr., 1976, vol. 32, no. 239.
- Kirzhinits, D.A., Lozovik, Yu.E., and Shpatakovskaya, G.V., Usp. Fiz. Nauk, 1975, no. 711, p. 3.
- Stash, A. and Tsirelson, V., WinXPRO A Program for Calculation of the Crystal and Molecular Properties Using The Model Electron Density, Moscow, 2001.
- 24. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T.A., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A., Gaussian 98, Revision A.9, 1998, Gaussian, Inc.: Pittsburgh PA.
- 25. Keith, T.A., AIMAll (Version 08.01.25), 2008, http://aim.tkgristmill.com.
- 26. Topchiev, A.V. and Fantalova, E.L., *Dokl. Akad. Nauk SSSR*, 1960, vol. 132, no. 3, p. 628.