Russian Journal of General Chemistry, Vol. 71, No. 3, 2001, pp. 429–436. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 3, 2001, pp. 466–472.

Synthesis and Structure of 1-Bromo-1-nitro-2-piperidino-(cyclohexylamino)-2-phenylethenes

E. A. Ishmaeva, V. M. Berestovitskaya, I. A. Litvinov,
Ya. A. Vereshchagina, E. G. Yarkova, G. R. Fattakhova,
D. B. Krivolapov, S. V. Makarenko, E. V. Trukhin, and I. V. Pavlova

Kazan State University, Kazan, Tatarstan, Russia
Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,
Russian Academy of Sciences, Kazan, Tatarstan, Russia
Herzen Russian State Pedagogical University, St. Petersburg, Russia

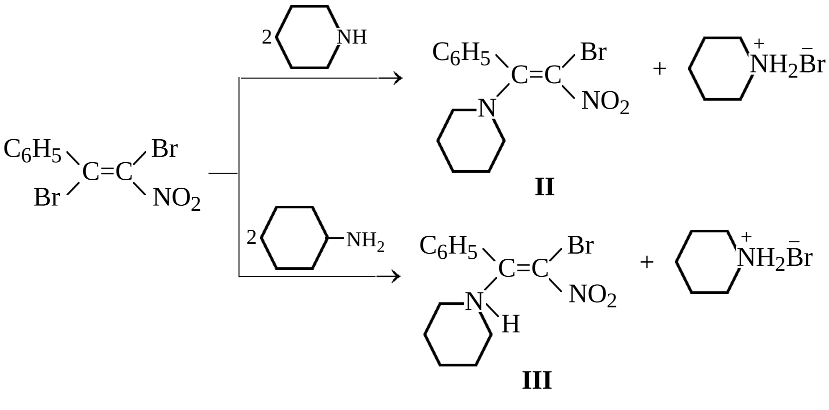
Received September 12, 2000

Abstract—A preparation method was developed for new representatives of halonitroenamines, 1-bromo-1-nitro-2-piperidino(cyclohexylamino)-2-phenylethenes. Both molecules possess *E* configuration and are of high polarity.

Nitroenamines containing in vicinal position amino and nitro groups attract attention both from practical and theoretical point of view (investigation on the specific features of the electronic structure of these molecules) [1–7]. In the nitroenamine series were found certain compounds with pronounced pharmacological properties [5]. Besides, now in the medical practice is widely applied antiulcer drug ranitidine that has a structure analogous to nitroenamines, a nitroketenaminal [6].

Halonitroenamines were mentioned in publications as unique examples [7–9], and they were as a rule obtained by difficult methods and in low (~30%) yields.

Basing on reaction of 1,2-dibromo-1-nitro-2-phenylethene (**I**) [10] with the corresponding amines we for the first time synthesized 1-bromo-1-nitro-2-piperidino(cyclohexylamino)-2-phenylethenes (**II, III**). The process occurs at boiling of compound **I** with double excess of amine in an anhydrous benzene for 2–3.5 h to afford the products of *S*N*Vin*-substitution **II** and **III** in 97 and 91% yield respectively.



II

III

Note that dibromonitrostyrene **I** reacts with amines under considerably more stringent conditions than the monohalonitrostyrenes with vicinal or geminal substituents [11–17]. This fact is apparently due to lower ste-ric accessibility of the reactive site C^2 and by steric hindrance to conjugation in the molecule of compound **I** since the nitro group deviates from the multiple bond

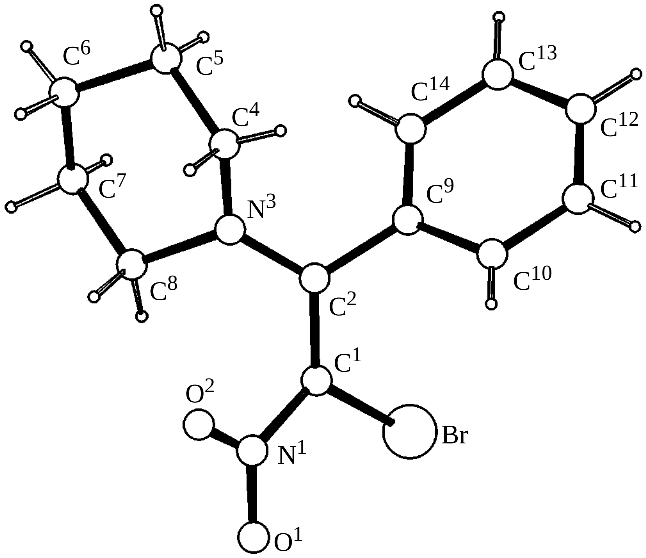


Fig. 1. Nitroenamine **II** molecular geometry in a crystal.

plane as was reliably shown by X-ray diffraction study [10].

The consideration of studies on the nitroenamines structure demonstrates that their geometry depends on the substituents and solvent character in a complicated way.

For instance, the X-ray diffraction study revealed that in the solid phase the 2-anilino-1-bromo-1-nitroethene has configuration with the trans-orientation of the NH and NO_2 groups [9]. It is known however that in quite a number of enamines with a secondary amino group the characteristic configuration corresponds to the *cis*-position of the amino and nitro groups. Therewith arises an intramolecular hydrogen bond $NH\cdots O_2N$ closing a quasi six-membered ring [12, 18–20]. Thus to 2-anilino-1-nitro-1,2-diphenylethene was assigned a *Z*-configuration (*cis*-position of the amino and nitro groups) [20] due to the independence of the amino group band in the IR spectrum of the concentration of the compound.

The most difficult is the assignment of configuration for the tetrasubstituted nitroenamines containing the amine rest with the tertiary nitrogen atom. In particular, from the UV spectral data for 2-morpholino-1-nitro-1,2-diphenylethene, namely from the position of the absorption band in the longwave region [λ_{max} 405–408 nm (ε 9700–9800)], was concluded [13] that in solutions was present the more energetically feasible and less sterically strained *E* isomer (*trans*-position of the amino and nitro groups). The X-ray diffraction study of the same compound demonstrated that it existed in the form of *Z* isomer (*cis*-position of the amino and nitro groups) [21].

The conclusions from [13, 21] made basing on UV spectroscopy and X-ray analysis suggest that 2-morpholino-1-nitro-1,2-diphenylethene in solution occurs in *E* configuration, and in the crystal state in *Z* configuration. It is quite reasonable since the *E* and *Z* isomers of nitroenamines as a rule have a relatively low barrier to isomeric transformations [22–24]. For instance, by means of ^1H, ^{13}C, and ^{14}N NMR spectroscopy [22] it was shown that α-nitro-β-amino-acrylic esters are sterically non-rigid in an extended set of solvents. This fact Bakhmutov *et al.* ascribed to the so-called “rotation around the double bond.”

We studied the structures of the new tetrasubstituted nitroenamines **II**, **III** by means of ^1H NMR, IR, and electronic spectroscopy, dipole moments, and X-ray diffraction analysis. In the ^1H NMR spectra of these compounds are seen all proton signals from structural fragments. For instance, the spectrum of compound **II** contains the resonances from the benzene ring protons (δ 7.60 ppm) and from the piperidine ring (δ 1.68 and 3.15 ppm); these data show its stereohomogeneity but do not reveal its geometry. The X-ray diffraction study of the piperidine derivative of bromonitrostyrene **II** definitely showed that its molecules in the solid phase possessed *E* configuration.

The spatial arrangement of compound **II** molecule is represented on Fig. 1, atom coordinates and geometrical parameters are listed in Tables 1–3. It should be noted that the double bond in the molecule is notably twisted [torsion angles $BrC^1C^2C^9$ 30.5(5) and $N^1C^1C^2N^3$ 36.6(6)°] (Table 3), bond length $C^1{=}C^2$ 1.399(6) Å (Table 2) is somewhat longer than that of nitroethene (1.337 Å) [25] or those of some substituted nitroethenes [26, 27]. On the contrary the bond $C^1–N^1$ [1.416(5) Å] is shorter than in the other nitroethanes (1.45–1.46 Å) [25–27]. Note that similar variations in bond lengths C=C (1.378 Å) and $C–NO_2$ (1.426 Å) are observed also in a molecule of another nitroenamine, 2-morpholino-1-nitro-1,2-diphenylethene [21]. Therewith the atoms C^1 and C^2 are sp^2-hybridized [the sum of bond angles at these atoms is equal to 359.9(4)°].

The nitro group at the C^1 atom is slightly turned with respect to the double bond plane: the torsion angle $O^2N^1C^1C^2$ is 9.1(6)°. The nitrogen atom of the piperidine substituent is of plane-trigonal coordination [the sum of bond angles is 359.3(3)°], but it is turned stronger with respect to the double bond plane: the torsion angle $C^1C^2C^9C^{10}$ is 47.9(5)°. The bond lengths $C^1–Br$ [1.879(4) Å] and $C^2–C^9(C_6H_5)$ [1.483(5) Å] have common values. The crystal structure of compound **II** is determined by van der Waals

Table 1. Coordinates of atoms in the structure of nitroenamine **II**, equivalent isotropic temperature factors of nonhydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i\, a_j)B(i,\ j)$ (Å^2), and isotropic temperature factors of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B* or B_{iso}
Br	0.03277(5)	0.20655(3)	0.24005(4)	2.826(8)
O^1	–0.1036(4)	0.3617(2)	0.2392(3)	4.33(8)
O^2	–0.1904(4)	0.3944(2)	0.0018(3)	3.36(7)
N^1	–0.1147(4)	0.3498(2)	0.1085(3)	2.74(8)
N^3	–0.0084(4)	0.3195(2)	–0.1457(3)	2.06(7)
C^1	–0.0446(5)	0.2798(2)	0.0794(4)	2.09(8)
C^2	–0.0367(4)	0.2635(2)	–0.0604(4)	1.93(8)
C^4	–0.0776(5)	0.3162(3)	–0.3132(4)	2.70(9)
C^5	0.0494(6)	0.3352(3)	–0.3764(4)	3.3(1)
C^6	0.1320(6)	0.4137(3)	–0.3144(5)	3.8(1)
C^7	0.2034(6)	0.4141(3)	–0.1431(5)	3.7(1)
C^8	0.0703(5)	0.3955(2)	–0.0843(4)	3.0(1)
C^9	–0.0492(5)	0.1810(2)	–0.1153(4)	2.14(8)
C^{10}	–0.1741(5)	0.1320(3)	–0.1125(4)	2.8(1)
C^{11}	–0.1875(6)	0.0558(3)	–0.1662(5)	3.8(1)
C^{12}	–0.0742(8)	0.0274(3)	–0.2195(6)	4.6(1)
C^{13}	0.0502(6)	0.0752(3)	–0.2217(5)	4.1(1)
C^{14}	0.0638(5)	0.1517(3)	–0.1690(4)	2.8(1)
H^{10}	–0.243(4)	0.148(2)	–0.087(4)	1.8(8)
H^{11}	–0.277(5)	0.024(2)	–0.162(4)	5(1)
H^{12}	–0.091(6)	–0.020(3)	–0.259(4)	5(1)
H^{13}	0.131(6)	0.057(3)	–0.250(5)	5(1)
H^{14}	0.152(5)	0.182(2)	–0.174(4)	3.0(9)
H^{41}	–0.126(5)	0.274(2)	–0.341(4)	3.2(9)
H^{42}	–0.160(4)	0.356(2)	–0.344(4)	2.4(9)
H^{51}	0.131(5)	0.294(2)	–0.339(4)	3.0(9)
H^{52}	–0.012(6)	0.341(3)	–0.488(5)	6(1)
H^{61}	0.215(5)	0.427(3)	–0.341(4)	4(1)
H^{62}	0.041(6)	0.460(3)	–0.361(5)	6(1)
H^{71}	0.289(5)	0.376(2)	–0.101(4)	4(1)
H^{72}	0.248(5)	0.463(2)	–0.098(5)	5(1)
H^{81}	0.111(5)	0.392(2)	0.019(4)	3.3(9)
H^{82}	–0.017(5)	0.439(2)	–0.109(4)	4(1)

Table 2. Bond lengths (*d*, Å) in the molecule of nitroenamine **II**

Bond	*d*	Bond	*d*
$Br–C^1$	1.879(4)	$C^6–H^{62}$	1.08(4)
$O^1–N^1$	1.234(5)	$C^7–C^8$	1.528(8)
$O^2–N^1$	1.230(4)	$C^7–H^{71}$	0.96(4)
$N^1–C^1$	1.416(5)	$C^7–H^{72}$	0.94(4)
$N^3–C^2$	1.342(5)	$C^8–H^{81}$	0.91(4)
$N^3–C^4$	1.471(5)	$C^8–H^{82}$	1.02(4)
$N^3–C^8$	1.468(5)	$C^9–C^{10}$	1.389(6)
$C^1–C^2$	1.399(6)	$C^9–C^{14}$	1.387(7)
$C^2–C^9$	1.483(5)	$C^{10}–C^{11}$	1.378(6)
$C^4–C^5$	1.510(7)	$C^{10}–H^{10}$	0.79(4)
$C^4–H^{41}$	0.82(4)	$C^{11}–C^{12}$	1.380(9)
$C^4–H^{42}$	0.94(3)	$C^{11}–H^{11}$	0.97(5)
$C^5–C^6$	1.518(7)	$C^{12}–C^{13}$	1.372(8)
$C^5–H^{51}$	0.96(4)	$C^{12}–H^{12}$	0.88(4)
$C^5–H^{52}$	0.99(4)	$C^{13}–C^{14}$	1.379(6)
$C^6–C^7$	1.503(6)	$C^{13}–H^{13}$	0.91(5)
$C^6–H^{61}$	0.89(5)	$C^{14}–H^{14}$	0.96(4)

contacts and by interactions of the type CH···O (weak hydrogen bonds) and $C^5–H^{52}\cdots O^1$ (*x, y, z* – 1). The parameters of bonds are as follows: $C^5–H^{52}$ 0.99(4), $C^5\cdots O^1$ 3.403(4), $H^{52}\cdots O^1$ 2.43(4) Å; angle $C^5–H^{52}\cdots O^1$ 168(5)°. Due to these interactions form endless chains along the *z* axis (Fig. 2). Short intramolecular contacts $C^8–H^{81}\cdots N^1$ and $C^8–H^{82}\cdots O^2$ are apparently forced by nitrogen atoms conjugation with the double bond.

Thus the data obtained (plane-trigonal coordination of the nitrogen atom in the piperidine substituent, changed bond lengths) evidence a significant electron density redistribution in compound **II** molecule.

We determined experimentally by Debye method [28] the dipole moments of nitroenamines **II**, **III** in benzene and dioxane at 25°C. The factors for calculation equations and orientation polarization are presented in Table 4. In calculation of dipole moments the values of bond angles were taken from the results of X-ray analysis of compound **II**, and also the following dipole moments of bonds and groups: $m(C_{sp^2}\rightarrow Br)$ 0.66 D calculated from $\mu_{exp}(CH_2{=}CHBr)$, $m(C_{sp^2}\rightarrow NO_2)$ 2.81 D from $\mu_{exp}(CH_2{=}CHNO_2)$, $m(Ph\rightarrow C_{sp^2})$ 0.33 D from $\mu_{exp}(C_6H_5CH{=}CH_2)$, $m(H\rightarrow N)$ 1.31 D from $\mu_{exp}(NH_3)$, $m(C_{sp^2}\rightarrow N)$ 2.12 D from $\mu_{exp}(C_6H_5NH_2)$, $m(cyclo\text{-}C_6H_{11}\rightarrow N)$ 1.06 D from $\mu_{exp}(cyclo\text{-}C_6H_{11}NH_2)$, $m(C_{sp^3}\rightarrow N)$ 1.02 D from μ_{exp}(piperidine), $m(C_{sp^2}\rightarrow N)$ 2.11 D from μ_{exp}(*N*-phenyl)piperidine. All experimental dipole moments of model compounds used in calculation of the moments for groups and bonds were taken from [29].

The study of the structure of bromonitroenamines **II**, **III** by dielcometry method revealed that the experimental values of their dipole moments are relatively large. The comparison of the experimental and calculated dipole moments does not allow determination of the *E* or *Z* isomer structure. Although the moments calculated for the *E*-forms are more alike

Table 3. Bond (ω, deg) and torsion (τ, deg) angles in the molecule of nitroenamine **II**

Angle	ω	Angle	ω	Angle	τ
$O^1N^1O^2$	122.5(4)	$C^6C^5H^{52}$	108.0(3)	$O^1N^1C^1Br$	7.95(0.51)
$O^1N^1C^1$	118.5(3)	$H^{51}C^5H^{52}$	119.0(4)	$O^1N^1C^1C^2$	–174.11(0.40)
$O^2N^1C^1$	119.0(3)	$C^5C^6C^7$	110.8(4)	$O^2N^1C^1Br$	–168.85(0.30)
$C^2N^3C^4$	122.8(3)	$C^5C^6H^{61}$	115.0(3)	$O^2N^1C^1C^2$	9.08(0.62)
$C^2N^3C^8$	123.5(3)	$C^5C^6H^{62}$	109.0(2)	$C^4N^3C^2C^1$	–148.44(0.40)
$C^4N^3C^8$	113.0(3)	$C^7C^6H^{61}$	106.0(2)	$C^4N^3C^2C^9$	35.35(0.56)
BrC^1N^1	115.7(3)	$C^7C^6H^{62}$	111.0(3)	$C^8N^3C^2C^1$	21.15(0.62)
BrC^1C^2	120.8(3)	$H^{61}C^6H^{62}$	105.0(4)	$C^8N^3C^2C^9$	–155.06(0.38)
$N^1C^1C^2$	123.4(3)	$C^6C^7C^8$	111.0(4)	$C^2N^3C^4C^5$	–134.06(0.41)
$N^3C^2C^1$	122.6(3)	$C^6C^7H^{71}$	112.0(3)	$C^8N^3C^4C^5$	55.37(0.48)
$N^3C^2C^9$	117.2(4)	$C^6C^7H^{72}$	114.0(3)	$C^2N^3C^8C^7$	133.92(0.39)
$C^1C^2C^9$	120.1(4)	$C^8C^7H^{71}$	107.0(3)	$C^4N^3C^8C^7$	–55.59(0.45)
$N^3C^4C^5$	112.6(3)	$C^8C^7H^{72}$	105.0(3)	$BrC^1C^2N^3$	–145.56(0.33)
$N^3C^4H^{41}$	109.0(3)	$H^{71}C^7H^{72}$	107.0(3)	$BrC^1C^2C^9$	30.54(0.53)
$N^3C^4H^{42}$	104.0(2)	$N^3C^8C^7$	110.1(4)	$N^1C^1C^2N^3$	36.61(0.63)
$C^5C^4H^{41}$	115.0(3)	$N^3C^8H^{81}$	107.0(2)	$N^1C^1C^2C^9$	–147.29(0.40)
$C^5C^4H^{42}$	110.0(3)	$N^3C^8H^{82}$	110.0(2)	$N^3C^2C^9C^{10}$	–135.76(0.39)
$H^{41}C^4H^{42}$	106.0(3)	$C^7C^8H^{81}$	113.0(3)	$N^3C^2C^9C^{14}$	44.67(0.52)
$C^4C^5C^6$	110.2(4)	$C^7C^8H^{82}$	113.0(3)	$C^1C^2C^9C^{10}$	47.93(0.54)
$C^4C^5H^{51}$	105.0(3)	$H^{81}C^8H^{82}$	103.0(3)	$C^1C^2C^9C^{14}$	–131.63(0.42)
$C^4C^5H^{52}$	106.0(3)	$C^2C^9C^{10}$	120.2(4)	$N^3C^4C^5C^6$	–53.54(0.47)
$C^6C^5H^{51}$	109.0(2)	$C^2C^9C^{14}$	120.6(4)	$C^4C^5C^6C^7$	54.43(0.52)
$C^{10}C^9C^{14}$	119.2(4)	$C^{11}C^{12}H^{12}$	117.0(4)	$C^5C^6C^7C^8$	–56.44(0.52)
$C^9C^{10}C^{11}$	120.2(5)	$C^{13}C^{12}H^{12}$	122.0(4)	$C^6C^7C^8N^3$	56.30(0.46)
$C^9C^{10}H^{10}$	121.0(2)	$C^{12}C^{13}C^{14}$	120.1(5)	$C^2C^9C^{10}C^{11}$	178.82(0.37)
$C^{11}C^{10}H^{10}$	119.0(2)	$C^{12}C^{13}H^{13}$	122.0(3)		
$C^{10}C^{11}C^{12}$	119.9(5)	$C^{14}C^{13}H^{13}$	118.0(3)		
$C^{10}C^{11}H^{11}$	117.0(3)	$C^9C^{14}C^{13}$	120.3(4)		
$C^{12}C^{11}H^{11}$	123.0(3)	$C^9C^{14}H^{14}$	124.0(2)		
$C^{11}C^{12}C^{13}$	120.3(4)	$C^{13}C^{14}H^{14}$	116.0(2)		

experimental values, still the difference between the calculated and measured values is too big: $\Delta\mu$ 3.9–4.4 D for compound **II** and 2,5–3.2 D for compound **III**. The results obtained evidence the high polarity of bromonitroenamines **II**, **III**, i.e. indicate the great contribution into their structure of bipolar form containing a $>C=\overset{+}{N}<$ bond and ionized nitro group (NOO^-) [2]. It is known that a contribution of bipolar forms considerably increases the dipole moments of organic compounds [2].

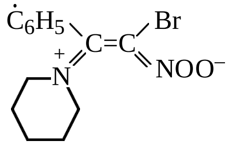
This conclusion is in agreement with the electron absorption spectra of compounds **II**, **III** containing absorption bands in the longwave region [compound **II**: λ_{max} 419 nm, (ε 12200); compound **III**: λ_{max} 373 nm, (ε 18400)]. The latter values are close to those for the model compound, 1-nitro-1,2-diphenyl-2-cyclohexylaminoethene with cis-position of cyclohexylamino and nitro groups (λ_{max} 375 nm, ε 20500) [18]. Therefore it is reasonable to suggest that nitroenamine **III** also possesses *E*-configuration.

The character of IR spectra of nitrostyrene **II** in solid phase and in chloroform solution is fairly alike. Therefore it is presumable that both in solution and solid phase compound **II** molecules are present in *E* configuration. Its IR spectra similarly to the spectra of previously described nitroenamines contain strong absorption bands in 1600–1500 cm^{-1} region that may be attributed to the system of conjugated multiple bonds with prevailing contribution from $>C=\overset{+}{N}<$ bonds. Also a number of bands is observed at 1264–1232, 1156–1120 cm^{-1} belonging to $>C=NOO^-$ moiety [1, 19, 20, 30–32]. The shift to lower frequencies of the bands from multiple bonds compared to the spectrum of *E*-2-bromo-1-(*p*-dimethylaminophenyl)-2-nitroethene [30] may be ascribed to appearance of the fourth substituent at the double bond

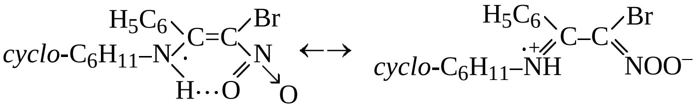
Table 4. Experimental and calculated dipole moments of nitroenamines **II, III**

Comp. no.	Solvent	α	γ	P_{or}, cm^3	μ_{exp}, D	μ_{calc}, D
II	C_6H_6	16.336	1.188	889.344	6.60	*E*: 2.70
	Dioxane	20.617	0.521	1027.239	7.09	*Z*: 2.29
III	C_6H_6	16.769	0.198	1012.938	7.04	ð: 4.51
	Dioxane	24.078	0.384	1212.386	7.70	*Z*: 2.64

(piperidino group) and its *cis*-orientation with respect to nitro group [33]. The observed spectral pattern characterizes the molecules of the compound under consideration as highly polarized, with a significant contribution from the stricture with separated charges.



In similar in character IR spectra of nitrostyrene **III** in mineral oil and in $CHCl_3$ is observed a weak absorption band at 3200 cm^{-1} belonging to NH group participating in a hydrogen bond; since the position and form of the band does not change at dilution of the solutions in $CHCl_3$ and benzene, it should originate from the intramolecular hydrogen bond NH···O_2N [34]. Therefore the NH and NO_2 groups in the molecules have *cis*-orientation, i.e. the molecules are of *E* configuration.



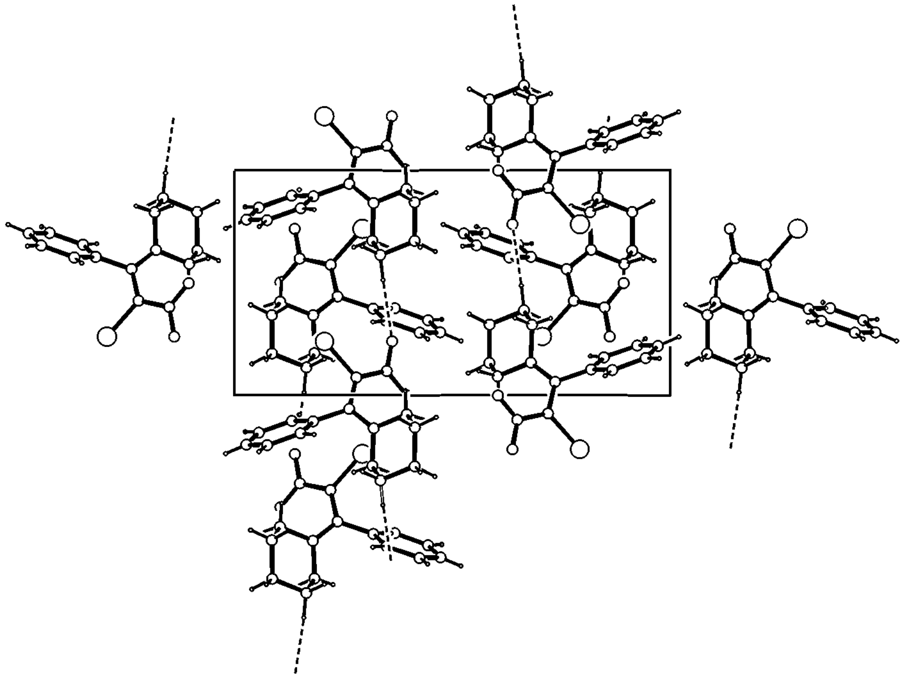


Fig. 2. Packing of nitroenamine **II** molecules in a crystal. Projection along 0– axis. Dotted lines show the hydrogen bonds C–H···O.

The absorption bands in the IR spectra of compound **III** in the 1600–1100 cm^{-1} region are somewhat different in position and intensity from those in the spectrum of compound **II**; however the general pattern of the spectrum is retained: strong bands at 1570–1562 cm^{-1} and a number of bands at 1350, 1220–1210, 1134–1124 cm^{-1} apparently originating from a system of conjugated multiple bonds and ionized nitro group NOO^{-}.

It should be noted that our assignments of the absorption bands in the IR spectra of compounds **II**, **III** are well consistent with the data described in [1, 19, 20, 30–32]. However the interpretation of the IR absorption bands of the nitroenamines in the literature is not always unambiguous. For instance, in [1] the absorption bands at 1530–1480 cm^{-1} were attributed to the N–O bond vibrations, and the bands at 1280–1230 cm^{-1} to $\nu_s(NO_2)$. The band at 1676 cm^{-1} according to the book [33] belonging to the absorption of the C=N bond, whereas in [35] the bands in the 1650–1550 cm^{-1} region are designated as "enamine bands." However irrespective of the difference in assignment of the bands to definite groups all the researchers make the same principal conclusion on the prevailing contribution into the ground state of the molecules of structures with separated charges.

Thus in the course of the study reported were developed convenient preparative procedures for the synthesis of new bromonitroenamines: 1-bromo-1-nitro-2-piperidino(cyclohexylamino)-2-phenylethenes. Their fine structure was investigated by means of X-ray diffraction analysis, dipole moments, IR, ^1H NMR, and electronic spectroscopy. We established *E* configuration and high polarization of the molecules of compounds studied originating from the efficient conjugation with participation of the lone pair of piperidine or cyclohexylamine nitrogen, carbon–carbon multiple bond, and nitro group.

EXPERIMENTAL

IR spectra were recorded on a Specord M-80 spectrophotometer (in solid phase, in chloroform, and in benzene solutions, concn. from 0.1 to 0.001 mol/l). ^1H NMR spectra were registered on spectrometers Bruker AC-200 (200 MHz), Tesla BS-487C (80 MHz) from solutions in $CDCl_3$; chemical shifts were measured either from internal reference (HMDS, TMS), or from external reference (HMDS), accuracy within ±0.5 Hz, δ scale. Electron absorption spectra were measured on spectrometer SF-46 in quartz cells, solvent acetonitrile.

Crystals of compound **II** monoclinic, mp 149–150°C, At 20°C *a* 8.823(2), *b* 16.955(3), *c* 9.594(2) Å; β 113.90(2)°, *V* 1312.2(5) $Å^3$, *Z* 4, d_{calc} 1.575 g/cm^3, space group $P2_1/c$. Unit cell parameters and intensities of 2933 reflections (11868 among them with $I \geq 3\sigma$) were measured on an automatic four-circle diffractometer Enraf-Nonius CAD-4 at 20°C (($\lambda M°K_\alpha$-irradiation, graphite monochromator, ω/2θ-scanning, $\theta \leq 29°$). In the course of the recording was no intensity decrease observed for three control reflections. The absorption was taken into account empirically (μMo 30.96 cm^{-1}). The structure was solved by heavy atom method. The bromine atoms coordinates were calculated from the peaks of the Patterson's function. After refining the latter in the isotropic approximation all the nonhydrogen atoms were revealed from the difference series of the electron density. The structure was refined first in isotropic and then in anisotropic approximation. After that from the difference series of the electron density were revealed all hydrogen atoms and finally refined in the isotropic approximation. The final values of divergence factors are as follows: *R* 0.037, R_W 0.047 from 1892 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried out with the use of program package MolEN [15] on the computer Alpha Station 200. The figures and analysis of intermolecular contacts in the crystal was performed along PLATON routine [20].

1,2-Dibromo-1-nitro-2-phenylethene (**I**) was prepared as described in [10].

1-Bromo-1-nitro-2-piperidino-2-phenylethene (II). A mixture of 0.61 g of nitrostyrene **I**, 0.4 ml of piperidine, and 10 ml of anhydrous benzene was refluxed for 2 h; during the process separated a precipitate. The mixture was cooled, the piperidine hydrochloride was filtered off, and the filtrate was poured into a Petri dish for evaporating the solvent. The residue was washed with distilled water. We obtained 0.59 g (97%) of compound **II**, mp 149–150°C (from methanol). IR spectrum, ν, cm^{-1}: 1512, 1418, 1294, 1264, 1232, 1208, 1152, 1120 (mineral oil); 1520, 1418, 1296, 1264, 1232, 1208, 1156, 1120 (chloroform). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.68, 3.15 ($C_5H_{10}N$), 7.60 (C_6H_5). UV spectrum (CH_3CN), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 419 (12200). Found, %: C 50.17, 50.22; H 4.89, 4.92; N 9.07, 9.08. $C_{13}H_{15}BrN_2O_2$. Calculated, %: C 50.18; H 4.82; N 9.01.

1-Bromo-1-nitro-2-phenyl-2-cyclohexylamino-ethene (III) was obtained in a similar way from 1.23 g of compound **I**, 0.97 ml of cyclohexylamine in 20 ml of anhydrous benzene (boiling for 3.5 h. We isolated 1.18 g (91%) of compound **III**, mp 161–163°C (from a mixture hexane–benzene, 1:1). IR spectrum, ν, cm^{-1}: 3200, 2370, 1676, 1568, 1562, 1412, 1350, 1320, 1210, 1124 (mineral oil); 3180, 2500, 1570, 1562, 1414, 1376, 1350, 1220, 1134, 1072 (chloroform). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.14–1.64, 2.96 (*cyclo*-$C_6H_{11}N$), 7.29 (C_6H_5), 11.05 (NH). UV spectrum (CH_3CN), λ_{max}, nm (ε, $l\,mol^{-1}\,cm^{-1}$: 373 [18400]. Found, %: C 51.73, 51.74; H 5.24, 5.26; N 8.71, 8.69. $C_{14}H_{17}BrN_2O_2$. Calculated, %: C 51.70; H 5.23; N 8.62.

ACKNOWLEDGMENTS

The study was carried out under financial support of the Program on Support of the Leading Scientific Schools (grants nos. 00-15-97424 and 96-15-97391) and of the Program “Russian Universities, Fundamental Research”)(grant no. 015.05.01.17)

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