Polarity and Structure of 2-(1-Methylbenzimidazol-2-yl)-1-phenyl- and -1,2-Diphenyl-1-nitroethenes

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Abstract—Polarity of 2-(1-methylbenzimidazol-2-yl)-1-phenyl- and -1,2-diphenyl-1-nitroethenes was determined and their structure was studied using electronic and ¹H, ¹³C NMR spectroscopy, dipole moments measuring, XRD analysis, and quantum-chemical calculations. It was shown that the 2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene has *Z*-configuration both in crystal and solution. The nitro group and benzimidazole substituent in its molecule are removed from the plane of the double bond. For 1,2-diphenyl-1-nitroethene *E*-structure is typical.

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It is known that nitrogen-containing heterocycles like indole, pyridine, and benzimidazole are potential holders of biological activity [1] and are widely distributed in nature. They are part of the molecules of many drugs: diazolin, cardiamine, indopan, dibazol, and others [2–5]. The convenient starting reagents for the synthesis of compounds containing the mentioned pharmacophoric heterocycles are the corresponding 2hetero-1-nitroethenes. Therefore, the study of structure and properties of 2-hetero-1-nitroethenes is an urgent task of modern organic chemistry.

We have previously investigated the structure of 2-(indol-3-yl)-, 2-(pyridin-3-yl)- and 2-(1-methylbenzimidazol-2-yl)-1-nitroethenes [6, 7]. These highly conjugated systems have the *E*-configuration, the molecules are almost flat.

This paper considers the disubstituted nitroalkenes: we first obtained and studied 2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I [8], as well as the previously known 1,2-diphenyl-1- nitroethene II [9] using a complex of physical methods and quantumchemical calculations. Nitroalkene with *N*-methylbenzimidazolyl substituent **I** was isolated as a mixture of *E*- and *Z*-isomers in a ratio of 5:1 from the synthesis carried out by method [8] that we somewhat modified. At the recrystalization of the *E*-isomer from acetone or alcohol it completely transformed into *Z*-isomer (Figs. 1, 2).



The Z-isomer is quite stable and does not change in time, while, unfortunately, we failed to separate the E-isomer from the mixture.

1,2-Diphenyl-1-nitroethene (nitrostylbene) II was prepared according to the method [9] that we slightly modified. It exists mainly as the E-isomer.

Fig. 1. ¹H NMR spectrum of (*Z*)-2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene **I.**

4.0

δ, ppm

7.0

8.0

NCH₃

CH=



Preference of the the Z-configuration in nitroalkene I and E in the case of II is connected, apparently, with lesser steric strain in these structures, and certain contribution from the conjugation of aromatic rings with the nitro group to the electronic organization of the molecule II in this geometric form.

The main test for assignment of the nitroalkene molecules under considerations to *E*- or *Z*-series is the chemical shift of olefinic protons signals in the ¹H NMR spectra: a downfield (8.17 ppm) shift of the olefinic proton signal of the *E*-isomer (in which this proton experiences a strong influence of the *cis*-located nitro group), and a shift of related signal to rather stronger field (6.82 ppm) in the spectrum of the *Z*-isomer in which the olefinic proton is removed from the nitro group and suffers obviously the anisotropic effect of the benzene ring [10, 11] (Table 1, Figs. 1, 2).

In the ¹³C NMR spectrum (Table 1) of the Z-isomer of compound I the signals of the carbon atoms in the olefinic fragment appear at 130.37 (C¹) and 106.14 ppm (C²), while in the spectrum of the *E*-form is observed a downfield shift of the C² signal (120.50 ppm). The correctness of interpretation of the ¹³C NMR spectra is confirmed using the methods of twodimensional heteronuclear correlation spectroscopy ¹H–¹³C HMQC and ¹H–¹³C HMBC (Figs. 3, 4). Thus,



Fig. 2. ¹H NMR spectrum of a mixture E:Z = 5:1 of the 2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I isomers.

in the ¹H–¹³C HMQC spectrum of the *Z*-nitroethene I (Fig. 3) there is a correlation between the olefinic proton H_A (6.82 ppm) and C² nucleus (106.14 ppm). A similar correlation is also found in the spectrum of *E*-forms: the cross-peaks between the proton H_A (8.17 ppm) and C² nucleus (120.50 ppm).

The validity of assignment of the chemical shifts of carbon atoms C¹ in the spectra of compounds I and II is confirmed using the method of ${}^{1}H{-}^{13}C$ HMBC. Thus, the ${}^{1}H{-}^{13}C$ HMBC spectrum of the Z-form of nitroethene I (Fig. 4) shows a correlation between the olefinic proton H_A (6.82 ppm) and carbon nucleus C¹ (130.37 ppm). A similar correlation is observed in the ${}^{1}H{-}^{13}C$ HMBC spectra between the proton H_A (8.17 ppm) and C¹ nucleus (130.33 ppm) for the *E*-forms.

To assess the polarity of the disubstituted nitroalkenes I and II we determined their dipole moments. The coefficients in the calculating equations and the orientational polarization are shown in Table 2.

Table 3 shows the values of dipole moments calculated by the vector-additive scheme and theoretical dipole moments of the investigated nitroethenes, as well as the relative energies of Z- and Eisomers. For convenience, the experimental values are repeated here. As is obvious from

Tables 2 and 3, polarities of the studied nitroethenes are quite high. Both compounds are brightly colored and have a limited solubility, therefore the dielectric permeabilities of both compounds were measured in dioxane, for compound **II** also benzene. The dipole Table 1. Spectral characteristics of 2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I and 1,2-diphenyl-1-nitroethene II



	R NO ₂											
.b. no	R	mp, °C	Yield,	δ_{H} , ppm, CDCl ₃		δ_{C} , ppm, CDCl ₃			Electronic spectra, in CH ₃ CN			
Com		C	,,,	R	H _A	Me	R, Ph	C^1	C^2	Me	λ _{max} , nm	3
Z-I	N N CH ₃	210–212	83	Bza: 7.30, 7.80 Ph: 7.50, 7.54;	6.82	3.87	109.42, 120.92, 123.07, 124.01, 125.88, 129.34, 131.30, 143.65, 144.21, 153.85	130.37	106.14	30.19	260 337	13000 37000
<i>E-</i> I		155–157 ^a	87	7.20–7.70	8.17	3.63	109.79, 121.06, 123.31, 124.58, 128.58, 130.74, 135.86, 154.91	130.33	120.50	30.63	352	23000
E-II	C ₆ H ₅	74–75	70	7.23, 7.50, 7.09, 7.33	8.23	_	128.83, 129.35, 130.18, 130.66, 130.89, 131.24, 131.28	149.71	134.97	_	226 ^b 318	10700 11000

^a The melting point is given for a mixture of E:Z = 5:1. ^b The figures for compound **II** are close to those published in [21, 22].

moment of the benzimidazole-containing nitroethene **I** could not be determined in benzene because of its low solubility.

For calculation of the dipole moments using the vector-additive scheme the values of bond angles

obtained by XRD analysis of 2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I were used (Table 4), as well as the following dipole moments of bonds and groups: $m(Ph-Csp^2) = 0.33$ D (calculated from μ_{exp} (CH₂=CHC₆H₅) [12]), $m(H-Csp^2) = 0.70$ D [13] m(Csp²-NO₂) = 2.81 D (calculated from the μ_{exp}



Fig. 3. ¹H–¹³C HMQC spectrum of (Z)-2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I.

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Fig. 4. ¹H–¹³C HMBC spectrum of (Z)-2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethene I.

(CH₂=CHNO₂) [12]), $m(\text{Het}-\text{Cs}p^2) = 3.34$ D (calculated from the μ_{exp} of *N*-methylbenzimidazole [12]).

Quantum-chemical calculations were carried out by HF [14] and hybrid DFT methods B3LYP and B3PW91 [15–17] using the basis set 6-31G(d) and 6-311++G(df,p) (Table 3) within Gaussian 03 software [18]. The simplest nonempirical HF method, as is

known, gives a fairly wide deviations of calculated geometric parameters from the experimental data. On the other hand, it reproduces experimental dipole moments somewhat better than DFT, as was shown in [19]. In turn, the DFT method gives some less consistent values of the dipole moments for these compounds, but agrees with the XRD data by the bond lengths and angles (Tables 4–6).

Table 2. The coefficients of the calculation equations and the orientation polarization of nitroethenes

Comp. no.	Solvent	α	γ	$P_{\rm or},{\rm cm}^3$	μ, D
Ι	Dioxane	24.669	2.045	1022.357	7.07
II	Benzene	16.868	1.345	656.895	5.67
	Dioxane	21.387	1.155	746.873	6.05

Table 3. Dipole moments (*D*) and relative energies (ΔE , kJ mol⁻¹) of *Z*- and *E*-isomers of 2-(1-methylbenzimidazol-2-yl)-1nitro-1-phenylethene I and 1-nitro-1,2-dphenylethene

Comp. no.	Isomer	μ_{calc} (vector)	µ _{exp} (benzene)	µ _{exp} (dioxane)	$\begin{array}{c} \mu_{theor} \\ B3PW91/ \\ 6\text{-}31G(d) \end{array}$	Δ <i>E</i> B3PW91/ 6-31G(d)	$\mu_{theor}B3PW91/6-311++G(df,p)$	Δ <i>E</i> B3PW91/ 6-311++G(df,p)	µ _{theor} HF/6-31G(d)	Δ <i>E</i> HF/6-31G(d)
Ι	Ε	5.94	-	7.07	5.01	0.0	5.40	0.0	4.99	0.0
	Ζ	3.63			6.48	11.4	6.73	9.5	6.90	8.4
II	Ε	2.93	5.67	6.05	5.35	0.0	5.60	0.0	5.75	0.0
	Ζ	3.51			3.32	14.4	3.52	13.1	3.99	13.5
		1	1							1

POLARITY AND STRUCTURE OF 2-(1-METHYLBENZIMIDAZOL-2-YL)-1-PHENYL-

Analysis of the data in Table 3 shows, firstly, that all used quantum-chemical methods reflect quite well reflect the polarity of the compounds and secondly, from the data follows that in the studied samples in each case one form (Z or E) predominantes.

Attention merits the high polarity of compound I: its μ_{exp} 7.7 D differs from the theoretical dipole moments and even more from the values calculated by the vector-additive scheme (5.94, 3.63 D). It is well known [20] that the simultaneous presence of the donor and acceptor groups in the vicinal positions of an unsaturated compound (in our case, the benzimidazole ring and the nitro group) can result in a significant increase in the experimental dipole moment in comparison with the μ_{calc} and μ_{theor} .

Note that for both compounds a considerable exaltation between experimental and calculated using vector-additive scheme dipole moments (both E- and Z-isomers) is observed. For the isomers of compound I it equals 1.13 and 3.44 D, respectively, for II, 3.12 and 2.54 D. Hence, the clear conclusion in favor of either isomer of compound I is unfortunately impossible from the dipole moments only. Such exaltation indicates the presence of electron density transfer in the unsaturated system in the direction of electronacceptor nitro groups. The moments of interaction calculated as the vector magnitudes at the direction from the benzimidazole ring to the nitro groups for compound I are equal to 3.16 D (μ_{exp} in dioxane 7.7 D) in E-isomer, and 3.47 D in the Z-isomer. For compound II the moments of interaction are, respectively: in the E-isomer from 4.3 D (experimental moment in benzene 5.67 D) to 3.48 D (μ_{exp} in dioxane 6.5 D), in the Z-isomer 3.63 D (benzene) and 3.4 D (dioxane). These are quite substantial values.

In addition to the above exaltation, the redistribution of electron density in both compounds was confirmed by the study of their electronic spectra. The electronic spectrum of Z-isomer of nitroalkene I contains a long-wavelength absorption band at λ_{max} 337 nm (ε 37 000 l mol⁻¹ cm⁻¹) (Table 1). The blue shift (15 nm) of this band compared with the similar band in the spectrum of *E*-form of I [λ_{max} 352 nm (23000)], as well as of the simplest analog, the (*E*)-2-(1-methylbenzimidazol-2-yl)-1-nitroethene [λ_{max} 367 nm (12000)] [6] points to the fact that at the realization of the *Z*-configuration of the molecule the conjugation is less effective due to the *cis*-arrangement of the nitro

Table 4. Bond angles (ω, deg) in molecule I

Angle	ω	Angle	ω
$C^3N^4C^5$	103.7(4)	$C^{14}C^{15}C^{16}$	120.0(7)
$C^{3}N^{11}C^{10}$	106.0(4)	$C^{15}C^{16}C^{17}$	119.3(6)
$C^{3}N^{11}C^{12}$	127.6(4)	$C^{16}C^{17}C^{18}$	121.3(6)
$C^{10}N^{11}C^{12}$	126.3(4)	$C^{13}C^{18}C^{17}$	119.9(6)
$O^{20}N^{19}O^{21}$	125.1(6)	$C^1C^2H^2$	117(4)
$O^{20}N^{19}C^1$	117.4(5)	$C^{3}C^{2}H^{2}$	115(3)
$O^{21}N^{19}C^{1}$	117.5(5)	$C^5C^6H^6$	121(5)
$N^{19}C^1C^2$	119.4(5)	$C^7 C^6 H^6$	122(5)
$N^{19}C^1C^{13}$	113.7(4)	$C^6 C^7 H^7$	116(5)
$C^{2}C^{1}C^{13}$	126.9(5)	$C^8C^7H^7$	122(5)
$C^1C^2C^3$	127.6(5)	$C^7 C^8 H^8$	123(5)
$N^{4}C^{3}N^{11}$	114.1(4)	$C^9C^8H^8$	114(5)
$N^4C^3C^2$	125.7(5)	C ⁸ C ⁹ H ⁹	121(5)
$N^{11}C^3C^2$	120.2(5)	$C^{10}C^{9}H^{9}$	122(5)
$N^4C^5C^6$	129.9(5)	$N^{11}C^{12}H^{121}$	102(4)
$N^{4}C^{5}C^{10}$	110.3(5)	$N^{11}C^{12}H^{122}$	109(5)
$C^{6}C^{5}C^{10}$	119.9(5)	N ¹¹ C ¹² H ¹²³	108(4)
$C^5C^6C^7$	117.3(6)	H ¹²¹ C ¹² H ¹²²	129(6)
$C^{6}C^{7}C^{8}$	122.1(6)	H ¹²¹ C ¹² H ¹²³	103(6)
$C^7 C^8 C^9$	121.5(5)	$H^{122}C^{12}H^{123}$	105(7)
$C^{8}C^{9}C^{10}$	116.6(6)	$C^{13}C^{14}H^{14}$	119(4)
$N^{11}C^{10}C^5$	105.8(4)	$C^{15}C^{14}H^{14}$	119(4)
$N^{11}C^{10}C^9$	131.6(5)	$C^{14}C^{15}H^{15}$	125(5)
$C^{5}C^{10}C^{9}$	122.6(5)	C ¹⁶ C ¹⁵ H ¹⁵	115(5)
$C^{1}C^{13}C^{14}$	120.2(5)	C ¹⁵ C ¹⁶ H ¹⁶	124(3)
$C^{1}C^{13}C^{18}$	121.6(5)	C17C16H16	117(3)
$C^{14}C^{13}C^{18}$	118.2(5)	$C^{16}C^{17}H^{17}$	126(5)
$C^{13}C^{14}C^{15}$	121.3(6)	C18C17H17	113(5)
$C^{13}C^{18}H^{18}$	121(3)	$C^{17}C^{18}H^{18}$	119(3)

group and the benzimidazole ring. The characteristics of compound **II** are close to literature data [21, 22].

As for the estimates of energy, the minimum energy for compounds I and II corresponds to the E-isomer (Table 3). While for compound **II** the energy preference of E-isomer is in agreement with the theo-retical values of the dipole moments obtained by different quantum-chemical methods (Table 3), the existence of compound I as the E-isomer is surprising since in it a substantial steric strain is expected. On the other hand, theoretical value of the dipole moment of Z-isomer of benzimidazole derivative I well repro-duces experimental dipole moment of this compound (Table 3). To understand this problem, we performed calculations of the model compound, 1,2-diphenyl-ethene (III). As expected, the minimum energy corresponds to the trans-isomer III, while the cis-isomer is less favorable by 20 kJ mol⁻¹. This fact suggests that nitro group can play an important role in reducing the energy for the E-

Table 5. Bond lengths (Å) in molecule I according to the XRD and the quantum-chemical calculations^a



Bond	XRD	B3PW91/6-31G(d)	B3LYP/6-31G(d)	B3PW91/6-31G(d) (dimer)	B3PW91/6-311++G(df,p)
O ²⁰ –N ¹⁹	1.226(8)	1.222 [0.004]	1.227 [0.001]	1.223 [0.003]	1.214 [0.012]
$O^{21} - N^{19}$	1.212(9)	1.217 [0.005]	1.222 [0.010]	1.218 [0.006]	1.211 [0.001]
$N^{4}-C^{3}$	1.321(7)	1.318 [0.003]	1.320 [0.001]	1.319 [0.002]	1.313 [0.008]
$N^{4}-C^{5}$	1.386(7)	1.371 [0.015]	1.375 [0.011]	1.373 [0.013]	1.368 [0.018]
$N^{11}-C^3$	1.363(7)	1.389 [0.026]	1.394 [0.031]	1.388 [0.025]	1.385 [0.022]
N^{11} - C^{10}	1.371(7)	1.378 [0.007]	1.383 [0.012]	1.378 [0.007]	1.375 [0.004]
N^{11} - C^{12}	1.462(7)	1.446 [0.016]	1.452 [0.010]	1.445 [0.017]	1.444 [0.018]
$N^{19}-C^{1}$	1.465(7)	1.480 [0.015]	1.486 [0.021]	1.478 [0.013]	1.484 [0.019]
$C^{1}-C^{2}$	1.332(8)	1.346 [0.014]	1.347 [0.015]	1.346 [0.014]	1.340 [0.008]
$C^{1}-C^{13}$	1.477(7)	1.469 [0.008]	1.472 [0.005]	1.469 [0.008]	1.465 [0.012]
$C^{2}-C^{3}$	1.458(7)	1.444 [0.014]	1.447 [0.011]	1.443 [0.015]	1.441 [0.017]
$C^{5}-C^{6}$	1.400(8)	1.402 [0.002]	1.403 [0.003]	1.403 [0.003]	1.397 [0.003]
$C^{5}-C^{10}$	1.399(7)	1.416 [0.017]	1.418 [0.019]	1.417 [0.018]	1.412 [0.013]
$C^{6}-C^{7}$	1.369(8)	1.386 [0.017]	1.389 [0.020]	1.386 [0.017]	1.382 [0.013]
$C^{7}-C^{8}$	1.398(10)	1.410 [0.012]	1.412 [0.014]	1.410 [0.012]	1.405 [0.007]
$C^{8}-C^{9}$	1.372(9)	1.389 [0.017]	1.392 [0.020]	1.389 [0.017]	1.385 [0.013]
C ⁹ -C ¹⁰	1.387(8)	1.396 [0.009]	1.398 [0.011]	1.396 [0.009]	1.392 [0.005]
C^{13} - C^{14}	1.388(8)	1.404 [0.016]	1.407 [0.019]	1.404 [0.016]	1.399 [0.011]
$C^{13}-C^{18}$	1.390(8)	1.404 [0.014]	1.407 [0.017]	1.404 [0.014]	1.399 [0.009]
C^{14} - C^{15}	1.376(8)	1.390 [0.014]	1.392 [0.016]	1.390 [0.014]	1.386 [0.010]
$C^{15} - C^{16}$	1.390(9)	1.395 [0.005]	1.397 [0.007]	1.395 [0.005]	1.390 [0.000]
$C^{16} - C^{17}$	1.358(11)	1.394 [0.036]	1.396 [0.038]	1.394 [0.036]	1.390 [0.032]
C^{17} - C^{18}	1.391(8)	1.391 [0.000]	1.393 [0.002]	1.391 [0.000]	1.386 [0.005]
		average [0.012]	average [0.014]	average [0.012]	average [0.011]

^a In brackets the difference is shown between the calculated and experimental values, in parentheses the error of experimental determination.

isomers of compounds I and II as compared with their Z-isomers. Unfor-tunately, it is impossible to reveal effective con-jugation in the molecules of these compounds based on the analysis of bond lengths: no significant changes are observed in the bond lengths C=C, =C-N, and =C-C< while comparing *E*- and *Z*-isomers of compounds I and II. It should be noted that most often reflection of conjugation on bond lengths occurs in the presence of a strong electron-releasing substituent in vicinal position to the nitro group, for

example, piperidino-, or *p*-dimethyl-amino-groups or electron-rich heterocycles indole, pyr-role, etc. [23].

Apparently, the effect of the energy reducing in I, as expected, is the result of a combination of electronic and steric factors. Indeed, in the case of Z-isomers, the nitro group is almost perpendicular to the plane of the double bond C=C, in the case of E-isomers they are coplanar. According to the method B3LYP/6-31G*, the angle of rotation of cyclic fragments in the *trans*

position to the nitro group [1-methylbenzimidazol-2-yl for I and phenyl for II] to the plane of the double bond is less in the *E*-isomer compared with Z isomers $(6^{\circ}/1^{\circ}$ in I, and $26^{\circ}/17^{\circ}$ in II). On the contrary, the aromatic ring in the *cis*-position to the nitro group further deviates from the plane of the double bond $(33^{\circ}/65^{\circ}$ in I and $32^{\circ}/57^{\circ}$ in II]; for III this value is 35°), which contributes to a substantial decrease in steric strain.

X-ray diffraction analysis of (Z)-2-(1-methylbenzimidazol-2-yl)-1-nitro-1-phenylethyl I indicates that this nitroalkene molecule in the crystal also has Z-configuration (Fig. 5). Tables 4–6 show the bond lengths, bond and torsion angles in the molecule of compounds I. Nitro group is substantially removed from the plane of the double bond: the torsion angles are $O^{20}N^{19}C^1C^2$ 75.9(7)° and $O^{21}N^{19}C^1C^2$ 105.5(6)°. The benzimidazole heterocycle is much less turned: angle $C^1C^2C^3N$ is 4 21.0(10)° and $C^1C^2C^3N^{11}$ is 161.8 (6)°. The rotation of the phenyl substituent is characterized by the torsion angles $N^{19}C^1C^{13}C^{18}$ 25.9(8)° and $C^2C^1C^{13}C^{14}$ 26.1(9)°.

Figures 6 and 7 show interactions and packing of the molecules in the crystal of compound **I**. The crystal packing can be described as stacking, the molecules in the stacks are arranged parallel. Between the layers there are C–H…O interactions involving hydrogen atom of benzimidazole ring and oxygen atom of the nitro group.

Consequently, the results of the performed experiment indicate the existence of 2-(1-methylbenz-imidazol-2-yl)-1-nitro-1-phenylethene I in solution and in solid phase as a Z-isomer. On the other hand, the correctness of the results of quantum-chemical calculations carried out by different methods and pointing to the minimum energy in the gas phase for the *E*-isomer, is also doubtless. By the way, in the synthesis this compound is formed preferably in the *E*-forms. There is a dual situation: on the one hand all the used physical methods confirm the Z-structure, on the other hand, a minimum of energy corresponds to the *E*-isomer.

In this regard, we can assume that this is a rare case of contribution of additional interactions in the preferred geometry of compound I that occur with the participation of the solvent or at the formation of crystal packing. In contrast to compound II, in the molecule (and in the crystal) of compound I the nitrogen atoms of the benzimidazole ring may play a certain role. It should be noted that the literature contains scarce data on the difference in the spatial structure of compounds in the crystal and solution (in particular, an example is 2-sila- and 2-phospha-1,3-

Table 6. Torsion angles in molecule I by the XRD data (τ , deg)

Angle	τ	Angle	τ
$C^3N^4C^5C^6$	180.0(6)	$C^{1}C^{2}C^{3}N^{11}$	-161.8(6)
$C^{3}N^{4}C^{5}N^{10}$	1.0(6)	$C^1C^2C^3N^4$	21.0(10)
$C^{5}N^{4}C^{3}N^{11}$	0.0(6)	$N^4C^5C^{10}N^{11}$	-1.6(6)
$C^5N^4C^3C^2$	177.4(5)	$C^{10}C^5C^6C^7$	1.3(8)
$C^{12}N^{11}C^{10}C^5$	179.7(5)	$C^{6}C^{5}C^{10}C^{9}$	-0.4(8)
$C^{3}N^{11}C^{10}C^{9}$	-178.9(6)	$N^4C^5C^{10}C^9$	178.8(5)
$C^{3}N^{11}C^{10}C^{5}$	1.5(6)	$C^{6}C^{5}C^{10}N^{11}$	179.3(5)
$C^{10}N^{11}C^3N^4$	-1.0(6)	$N^{4}C^{5}C^{6}C^{7}$	-177.6(6)
$C^{12}N^{11}C^3N^4$	-179.1(5)	$C^{5}C^{6}C^{7}C^{8}$	-1.5(10)
$C^{10}N^{11}C^3C^2$	-178.5(5)	$C^{6}C^{7}C^{8}C^{9}$	0.7(11)
$C^{12}N^{11}C^3C^2$	3.4(8)	$C^{7}C^{8}C^{9}C^{10}$	0.3(10)
$C^{12}N^{11}C^{10}C^9$	-0.7(10)	$C^{8}C^{9}C^{10}C^{5}$	-0.5(9)
$O^{21}N^{19}C^1C^{13}$	73.8(7)	$C^{8}C^{9}C^{10}N^{11}$	180.0(6)
$O^{20}N^{19}C^1C^{13}$	-104.9(6)	$C^{1}C^{13}C^{18}C^{17}$	178.3(6)
$O^{20}N^{19}C^1C^2$	75.9(7)	$C^{18}C^{13}C^{14}C^{15}$	1.3(9)
$O^{21}N^{19}C^1C^2$	-105.5(6)	$C^{1}C^{13}C^{14}C^{15}$	-179.6(6)
$C^{2}C^{1}C^{13}C^{14}$	26.1(9)	$C^{14}C^{13}C^{18}C^{17}$	-2.6(9)
$N^{19}C^1C^{13}C^{18}$	25.9(8)	$C^{13}C^{14}C^{15}C^{16}$	0.2(11)
$N^{19}C^{1}C^{2}C^{3}$	4.7(9)	$C^{14}C^{15}C^{16}C^{17}$	-0.4(11)
$C^{13}C^{1}C^{2}C^{3}$	-174.5(5)	$C^{15}C^{16}C^{17}C^{18}$	-1.0(11)
$C^{2}C^{1}C^{13}C^{18}$	-154.9(6)	$C^{16}C^{17}C^{18}C^{13}$	2.5(11)
$N^{19}C^1C^{13}C^{14}$	-153.1(5)		

dioxa-6-aza-cycloethanes), indicating that the configuration (or conformation), in crystal is not necessarily retained in solution [24].

Obviously, in the case of I the estimated value of the minimum energy for the *E*-isomer does not prove that just the *E*-isomer must exist. However, this problem certainly requires further detailed study.

Thus, as a result of a complex study performed (¹H and ¹³C NMR and electronic spectroscopy, dipole moments, XRD analysis, and quantum-chemical calculations) the fine structure of substituted nitroethenes, 2-(1-methylbenzimidazol-2-yl)-1-phenyl- and 1,2-diphenyl-1-nitroethenes was studied, the polarity was revealed, the geometry was determined, and for the benzimidazole derivative the conformational features were analyzed in the arrangement of the substituents at the carbon–carbon double bond.

EXPERIMENTAL

¹H, ¹³C-{¹H}, ¹H-¹³C HMQC, and ¹H-¹³C HMBC NMR spectra were obtained on a Jeol ECX400A spectrometer [400 MHz (¹H), 100 MHz (¹³C)].



Fig. 5. Geometry of the molecule I in crystal.



Fig. 6. C–H…O interactions in crystals of I.

Chloroform- d_1 was used as a solvent, the signal of residual protons of the solvent were used as internal reference. The electron absorption spectra were recorded on a Shimadzu UV2401PC spectrophotometer using quartz cells, solvent acetonitrile.

To determine the experimental values of dipole moments the second Debye method was applied, which is based on measuring the dielectric permeability of dilute solutions of substances in a nonpolar solvent [25]. The solvent for measuring dielectric permeability of solutions of I was dioxane, for compound II benzene and dioxane. Measurements were carried out at 25°C on a BI-870 instrument (Brookhaven Instruments Corporation), the accuracy was ± 0.01 . The coefficients of equations for the calculations and the orientational polarization are listed in Table 2. The refractive indices of solutions were determined on a RA-500 refractometer (Kyoto Electronics), the accuracy was ± 0.0001 . Quantum-chemical calculations by HF [14] and hybrid DFT methods B3LYP and B3PW91 [15–17] were performed using the 6-31G(d) and 6-311++G(df, p) basis sets (Table 3) with the Gaussian 03 software [18]. The correspondence of the found stationary points to the minima was proved by calculation of second derivatives. In all cases the ownvalues of the Hessian matrix were positive.

The calculations were performed in the Kazan branch of the Joint Supercomputer Center of Russian Academy of Sciences (http://wt.knc.ru).

XRD analysis of a single crystal of compound **I** was performed at the Department of diffraction of the Multiple-access Center for collective use at the Laboratory of diffraction research methods in the Arbuzov Institute of Kasan Scientific Center of Russian Academy of Sciences.

Crystals of I were obtained by crystallization from acetone. Composition $C_{16}H_{13}N_3O_2$, *M* 279.29, mono-



Fig. 7. Packing of molecules of I in the crystal.

clinic. At 20°C, a = 7.469(5), b = 6.566(4), c = 27.92(2) Å, $\beta = 94.500(8)^{\circ}$, V = 1364(2) Å³, $d_{calc} = 1,359$ g cm⁻³, Z = 4, space group $P2_1/c$.

The cell parameters and intensities of 10202 reflections, of which 2723 were independent with $I \ge 2\sigma$ $(R_{int} = 0.0603)$ were measured on a Bruker Smart Apex II CCD automatic diffractometer (Mo K_{α} radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω -scanning, measuring range: $-9 \le h \le 9, -8 \le k \le 8, -34 \le l \le 34$, $2.20^{\circ} \le \theta \le 26.00^{\circ}$). The extinction was accounted for semiempirically using the SADABS software [26] $(\mu Cu = 0.93 \text{ cm}^{-1})$. The structure was solved by the direct method and refined by least-squares method initially in isotropic, then in anisotropic approximation (for all non-hydrogen atoms), using the SHELXTL [27] and WinGX [28] software. The hydrogen atoms were revealed from the difference series of electron density and refined isotropically. The final values of divergence factors are: R = 0.1071, $R_w = 0.2905$ for 2723 independent reflections with $F^2 \ge 4\sigma$, GOOF =1.108, number of refined parameters 244. Collection, indexing, and data processing were performed with the APEX2 software [29]. Analysis of intermolecular interactions of molecules and figures were made using the PLATON software [30]. The coordinates of atoms of the structure and their temperature parameters are deposited in the Cambridge database of crystal data.

The initial 2-hydroxy-2-(methylbenzimidazol-2-yl)-1-nitro-1-phenylethane was synthesized according to the procedure [8].

2-(1-Methylbenzimidazol-2-yl)-1-nitro-1-phenylethene (I). To 1.1 g of 2-hydroxy-2-(methylbenzimidazol-2-yl)-1-nitro-1-phenylethane 2.6 ml of acetic anhydride were added, and the reaction mixture was heated under stirring for 30 min in a boiling water bath until complete dissolution of the precipitate. Then 20.2 ml of ice water were added and the stirring was continued for 2 h. The precipitate formed was filtered off, washed on the filter with water, alcohol, and ether, and dried in air. The substance I was obtained as a mixture of isomers, E:Z = 5:1. Yield 0.9 g (87%), mp 155–157°C. The mixture of isomers was recrystallized from 50 ml of methanol. At a short-term boiling the methanolic solution in the process of recrystallization E-Z isomerization occurred. Yield of I-Z isomer 0.86 g (83%), mp 210–212°C (from methanol).

1,2-Diphenyl-1-nitroethene II. The reaction mixture consisting of 2 ml of methanol, 5.6 ml phenylnitromethane, 0.23 g of methylamine hydrochloride, 0.07 g of sodium hydrogen carbonate, and 4.8 ml of benzaldehyde, was stirred at 18–20°C for 72 h. The resulting precipitate was filtered off and washed on the filter with methanol. Yield of **II** 7.5 g (70%), mp 74– 75°C (from methanol). (published mp 74–75°C [9]).

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