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Conformational Analysis of 2-Substituted 1-Nitro- and 1-Bromo-1-nitroethenes

E. A. Ishmaeva[a], A. A. Gazizova[b], Ya. A. Vereshchagina[a, b], D. V. Chachkov[b], N. A. Anisimova[c], S. V. Makarenko[c], A. S. Smirnov[c], and V. M. Berestovitskaya[c]

[a] *Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia*
e-mail: Eleonora.Ishmaeva@ksu.ru
[b] *Kazan State Technological University, Kazan, Tatarstan, Russia*
[c] *Hertzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia*

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Abstract — Conformational analysis of 2-trichloromethyl(ethoxycarbonyl)-1-nitro- and 2-trichloromethyl-(ethoxycarbonyl)-1-bromo-1-nitroethenes was performed using the dipole moment method, IR spectroscopy, and DFT quantum-chemical calculations (B3LYP/6-31G*). The nitro and ester (or trichloromethyl) groups in the molecules of these compounds were found to occupy *trans* positions with respect to the double C=C bond, i.e., the nitroalkenes have *E*, and their bromine-containing analogs, *Z* configuration; the compounds having an ethoxycarbonyl group are characterized by *s-cis* orientation of the C=C and C=O bonds.
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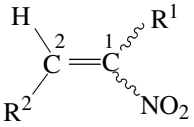
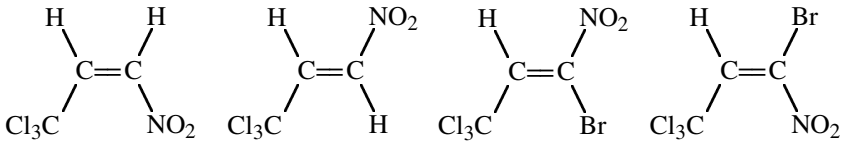
The interest in the steric and electronic structure and reactivity of functionally substituted conjugated nitroethenes originates from their application as convenient models for studying general theoretical problems of organic chemistry [1–4], as well as from their utility as starting materials for the synthesis of practically important compounds, such as drugs, pesticides, structural fragments of naturally occurring substances, etc. For example, the first Russian tranquilizer Fenibut which is now widely used in medical practice [5, 6] was synthesized on the basis of β-nitrostyrene. An elegant synthesis of the natural alkaloid Mesembrane possessing narcotic and anticarcinogenic properties was performed via Diels–Alder condensation of 2-(3,4-dimethoxyphenyl)-1-nitroethene with buta-1,3-diene and subsequent transformations of the adduct [7]. In the present article we report on the results of experimental and theoretical conformational analysis of 2-substituted 1-nitro- (**I, III**) and 1-bromo-1-nitroethenes (**II, IV**) using the dipole moment method, IR spectroscopy, and quantum-chemical calculations in terms of the hybrid density functional theory (DFT B3LYP/6-31G*).



I–IV

I, R^1 = H, R^2 = CCl_3; **II**, R^1 = Br, R^2 = CCl_3; **III**, R^1 = H, R^2 = EtOCO; **IV**, R^1 = H, R^2 = EtOCO.

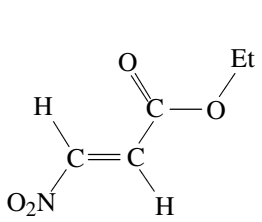
The structures of the *Z* and *E* isomers of nitroethenes **I** and **II** are shown below.



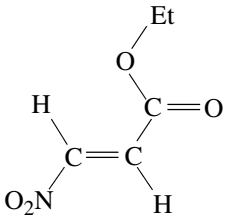
Z *E* *Z* *E*

The relative energies and theoretical and experimental dipole moments of compounds **I** and **II**, as well as those calculated by the vector-additive scheme, are given in Table 1. It is seen that the experimental dipole moments of nitroethenes **I** and **II** approach the vector-additive values calculated for the *E* isomer of **I** and *Z* isomer of bromonitroethene **II**. The theoretical (DFT B3LYP/6-31G*) dipole moments, too, reproduce fairly well the polarity of these compounds. In addition, the above isomers have the lowest energies. Therefore, we can conclude that 1-nitro-2-(trichloromethyl)ethene (**I**) and 1-bromo-1-nitro-2-(trichloromethyl)ethene (**II**) exist as isomers with *trans* arrangement of the NO_2 and CCl_3 groups, i.e., compound **I** has *E* configuration, and **II** is *Z* isomer.

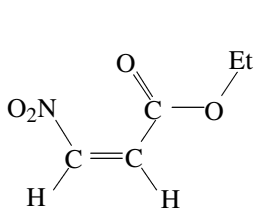
The structures of possible isomers and conformers of substituted nitroethenes **III** and **IV** having an ethoxycarbonyl group are shown below.



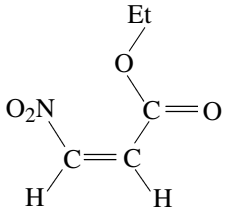
E-s-cis



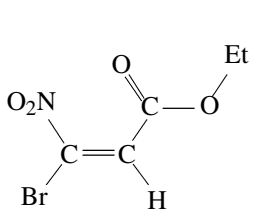
E-s-trans



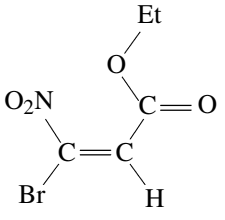
Z-s-cis



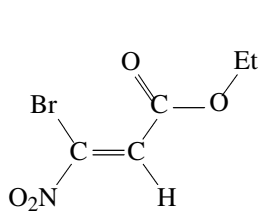
Z-s-trans



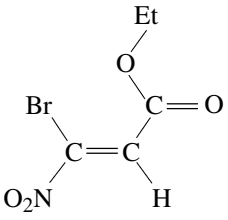
E-s-cis



E-s-trans



Z-s-cis



Z-s-trans

Table 2 contains the relative energies and experimental, theoretical (ν_{theor}, B3LYP/6-31G*), and vector-additivity (ν_{calc}) dipole moments of different isomers and conformers of compounds **III** and **IV**. The minimal energies correspond to the *E-s-cis* conformer of **III** and *Z-s-cis* conformer of **IV**. The μ_{theor} and μ_{calc} values are well consistent with the experimental dipole moments of these conformers. However, the dipole moments of the *E-s-cis* and *E-s-trans* conformers of **III** are fairly similar, and it is difficult to make unambiguous choice on the basis of these data. On the other hand, the *E-s-trans* structure is less energetically favorable than *E-s-cis*. As concerns the rotational isomerism arising from rotation of the

Table 1. Relative energies and theoretical (μ_{theor}, B3LYP/6-31G*), calculated by the vector-additivity scheme (μ_{calc}), and experimental (μ_{exp}) dipole moments of the *Z* and *E* isomers of compounds **I** and **II**

Comp. no.	Isomer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
I	*Z*	8.76	3.43	4.23	2.08
	E	0	2.24	2.25	
II	*Z*	0	1.58	1.97	1.92
	E	6.11	2.89	3.43	

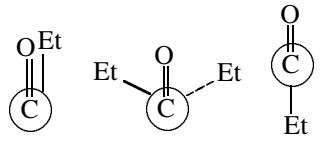
Table 2. Relative energies and theoretical (μ_{teor}, B3LYP/6-31G*), calculated by the vector-additivity scheme (μ_{calc}), and experimental (μ_{exp}) dipole moments of the *Z* and *E* isomers of compounds **III** and **IV**

Comp. no.	Conformer	ΔE, kcal mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
III	*E-s-cis*	0	4.61	2.93	2.99
	E-s-trans	0.66	4.34	2.67	
	Z-s-cis	Not found		5.50	
	Z-s-trans	5.73	3.56	3.72	
IV	*E-s-cis*	4.46	4.68	4.95	3.45
	E-s-trans	4.24	3.05	2.39	
	Z-s-cis	0	3.94	3.60	
	Z-s-trans	1.41	4.17	1.46	

Table 3. Characteristic vibration frequencies in the IR spectra of 2-substituted 1-nitro- and 1-bromo-1-nitroethenes **I**–**IV**

Experimental frequency, cm^{-1}								Assignment
I		**II**		**III**		**IV**		
neat	CH_2Cl_2	neat	CH_2Cl_2	neat	CH_2Cl_2	neat	CH_2Cl_2	
3119 m	3119 m	–	–	3111 m	3113 m	–	–	$\nu_{anti}(CH)$
3064 m	3062 m	3061 m	3063 m	3083 m	3082 m	3068 m	3067 m	$\nu_{syn}(CH)$
–	–	–	–	2987 m	2987 m	2986 m	2986 m	
–	–	–	–	2943 w	2943 w	2941 w	2941 w	$\nu(CH_3)$
–	–	–	–	2908 w	2906 w	2908 w	2907 w	
–	–	–	–	2880 w	2880 w	2874 w	2874 w	$\nu(CH_2)$
–	–	–	–	1731 v.s	1731 v.s	1734 v.s	1735 v.s	ν(C=O)
1659 w	1658 w	1620 m	1621 m	1646 m	1645 m	1631 m	1631 m	ν(C=C)
1542 v.s	1543 v.s	1557 v.s	1558 v.s	1541 v.s	1541 v.s	1558 v.s	1560 v.s	$\nu_{as}(NO_2)$
–	–	–	–	1469 m	1467 w	1468 w	1472 w	
–	–	–	–	1446 m	1446 w	1444 w	1444 w	$\delta(CH_3)$
–	–	–	–	1396 m	1398 w	1393 w	1392 w	$\delta(CH_2)$
–	–	–	–	1369 m	1371 m	1369 m	1369 m	
1358 s	1358 s	1318 s	1318 s	1357 s	1356 s	1325 m	1325 m	$\nu_s(NO_2)$
–	–	–	–	1305 s	1305 s	1305 s	1306 s	
				1178 s	1178 s	1187 s	1188 s	ν(COC)
–	–	–	–	1034 s	1034 s	1026 s	1026 s	ν(O–C)
974 m	974 m	–	–	951 s	950 s	–	–	
–	–	866 s	868 s	–	–	930 w	931 w	ω(=CH)
–	–	–	–	860 m	860 m	882/862 m	884/862 m	ν(O–C)
766 s	–	764 s	–	–	–	–	–	
609 m	609 m	626 m	626 m	–	–	–	–	ν_{as}(C–Cl)
–	–	592 m	591 m	–	–	687 m	–	ν(C–Br)

ethyl group about the C_{sp^2}–O bond in **III**, the experimental dipole moment of this compound (Table 2) corresponds to noneclipsed *gauche*$_1$ and *gauche*$_2$ conformers (μ 2.93 and 2.67 D, respectively). The concentration of the *trans* conformer (μ 2.77 D) is negligible, if at all. The experimental dipole moment of nitroethene **IV** (Table 2) also corresponds best to conformers with *gauche* orientation of the ethyl and carbonyl groups (μ 3.60 and 3.78 D, respectively), while the dipole moment of the *s-trans* structure exceeds both the experimental value (by 0.7 D) and those calculated for the *gauche* conformers. Possible orientations of the ethyl group with respect to the C=O bond in molecules **III** and **IV** are illustrated below by Newman projections.



cis *gauche*$_1$, *gauche*$_2$ *trans*

The good agreement between the experimental and calculated dipole moments of the nitroethenes under study led us to conclude that, unlike strongly polar 1-bromo-1-nitro-2-piperidino(cyclohexylamino)-2-phenylethenes (μ 7.0 D) [8] and indolylnitroethenylphosphonates (μ 7.0 D) [9], the molecules of 2-trichloromethyl(ethoxycarbonyl)-1-nitro- and 2-trichloromethyl(ethoxycarbonyl)-1-bromo-1-nitroethenes **I**–**IV**, as well as bis(2-chloroethyl) 2-nitroethenylphosphonates [10], lack appreciable electronic interactions. To characterize fine structure of the compounds under study, we examined their IR spectra which were recorded from liquid samples placed between KBr plates and solutions in methylene chloride. The vibration frequencies are given in Table 3. Some specificity of stretching and bending vibrations of bonds and groups of atoms and their intensities should be noted. In particular, the region of =C-H stretching vibrations attracts interest. Unlike trisubstituted ethenes **II** and **IV**, the spectra of disubstituted compounds **I** and **III** contain two absorption bands in that region, which belong to syn- and antiphase vibrations of two C–H bonds (Table 3). According to published data [11, 12],

1,2-disubstituted vinyl derivatives (even those containing halogen atoms) give rise to onlyone absorption band at 3050–3000 cm^{-1}. The presence of two separate C–H bonds in the IR spectra of **I** and **III** is likely to result from the presence in their molecules of two strongly electron-withdrawing groups. Another interesting fact was revealed while analyzing the IR spectra of 1-bromo-1-nitroethenes **II** and **IV**. Stretching vibrations of the C–Br bond is not characteristic. Like ν(C–Cl), ν(C–Br) bands are obscured by a number of bending vibration bands; therefore, the C–Br vibration frequency is quite unreliable from the viewpoint of assignment of empirical parameters. On the other hand, the bromine atom strongly affects vibrations of the neighboring NO_2 group. As a result, the asymmetric vibration frequency of the nitro group $\nu_{as}(NO_2)$ increases and $\nu_s(NO_2)$ decreases [12]; this is clearly observed in the IR spectra of compounds **II** and **IV** ($\Delta\nu$ = 230–240 cm^{-1}; Table 3).

Analysis of the IR spectra of nitroethenes **I**–**IV** allowed us to draw some conclusions concerning their steric structure. The presence in the spectra of 2-substituted 1-nitroethenes **I** and **III** of an absorption band at 970–950 cm^{-1}, corresponding to out-of-plane bending vibrations of the =C–H bonds [ω(=CH)], suggests *trans* configuration of the double bond in their molecules. As might be expected, no analogous bands were observed in the spectra of trisubstituted ethenes **II** and **IV**.

The IR spectra also provide information on the mutual orientation of the C=C bond and carbonyl group. As shown in [13], interaction between C=C and C=O vibrations in some α,β-unsaturated ketones (e.g., mesityl oxide and some cyclic α,β-unsaturated ketones) could lead to anomalous intensity redistribution of the Raman and IR bands, while intensity distribution of the IR bands in the spectrum of *s-trans* conformers is similar to that observed for compounds with isolated C=C and C=O bonds. Just the latter pattern is typical of the IR spectra of nitroethenes **III** and **IV**. It should be noted that the relations described in [13] are inherent to vinyl ketones containing no other functional groups; therefore, it seems to be inappropriate to apply them to the subjects of our study. In addition, the results of this test are not consistent with those obtained on the basis of dipole moments and theoretical calculations.

Thus, using the dipole moment method, IR spectroscopy, and quantum-chemical calculations, we have found that the molecules of 1-nitro-2-trichloromethyl-(ethoxycarbonyl)ethenes and 1-bromo-1-nitro-2-trichloromethyl(ethoxycarbonyl)ethenes are characterized by *trans* orientation of the nitro and trichloromethyl (or ester) groups, i.e., compounds **I** and **III** are *E*, while **II** and **IV** are *Z* isomers, and that the C=C and C=O bonds in nitroacrylates are arranged *s-cis*.

Table 4. Coefficients in the equations used in the calculations, orientational polarizations, and experimental dipole moments of compounds **I**–**IV**

Comp. *no.*	α	γ	P_{or}, cm^{-1}	μ_{exp}, *D*
I	2.561	0.084	88.742	2.08
II	1.596	0.107	75.264	1.92
III	6.676	–0.009	182.341	2.99
IV	5.762	–0.013	243.306	3.45

EXPERIMENTAL

Synthesis 3,3,3-trichloro-1-nitropropene (**I**) and 1-bromo-3,3,3-trichloro-1-nitropropene (**II**) were synthesized by the procedures described in [14] and [15], respectively. Ethyl 3-nitroprop-2-enoate (**III**) was prepared according to a modified Shechter procedure [16, 17], and ethyl 3-bromo-3-nitroprop-2-enoate (**IV**) was obtained as described in [18]. Samples of **I**–**IV** had the following boiling points: **I**, 82–83°C (10 mm); **II**, 105–107°C (10 mm); **III**, 85–95°C (8–10 mm); **IV**, 109–112°C (10 mm).

The dipole moments of compounds **I**–**IV** were measured in benzene at 25°C according to [19]. In the calculation of dipole moments by the vector-additive scheme we used the following bond angles: ∠CCBr 121° [20], ∠CC=O 120°, ∠CCO 120°, ∠CCH 121° [21], $\angle CCH^1$ 118° [21], $\angle CCH^2$ 117° [21], and bond and group moments: $m(C_{sp^2}–Br)$ = 0.66 D (calculated from μ_{exp} of CH_2=CHBr [22]), $m(C_{sp^2}–NO_2)$ = 2.81 D (calculated from μ_{exp} of CH_2=$CHNO_2$ [22], $m(H–C_{sp^2})$ = 0.70 [23]; the group moment $m(CCl_3)$ = 1.26 D was calculated from the experimental dipole moment of 1,1,1-trichloroethane [24], the bond moment $m(C_{sp^3}–C_{sp^2})$ = 0.78 D was calculated from μ_{exp} of C_3H_6 [22], *m*(C=O) = 1.94 D [25], *m*(C–O) = 0.18 D (calculated from μ_{exp} of EtOAc), and *m*(Et–O) = 1.11 D [22].

The coefficients in the equations used in the calculations, orientational polarizations, and experimental dipole moments are given in Table 4. Benzene was purified by standard procedure [26]. The IR spectra of compounds **I**–**IV** were recorded in the range from 4000 to 400 cm^{-1} on a Bruker Vector-22 spectrometer with Fourier transform (resolution 1 cm^{-1}; layer thickness 0.023 cm; concentration 4×10^{-2} M for **I** and **II**, 1×10^{-1} M for **III**, and 3×10^{-3} M for **IV**).

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