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On the 100th anniversary of V.V. Perekalin

Polarity and Structure of α-Nitrocinnamic Acid Esters

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Abstract—Polarity and structure of ethyl α-nitrocinnamates have been studied by means of dipole moments method and quantum-chemical calculations. These compounds exist in the form of *Z*-isomers in solution, that is, nitro group and benzene ring are *cis*-positioned.

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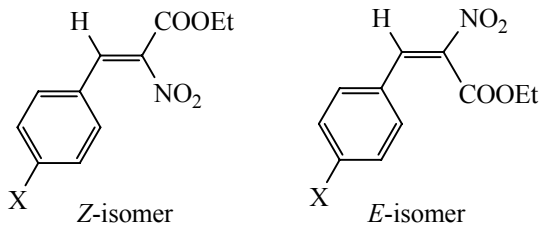
Conjugated nitroethenes and their functionalized analogs are readily available reactive compounds that can be converted into the practically important linear and cyclic structures [1, 2]. Therefore, the study of the structure and properties of such compounds is an important topic of modern organic chemistry.

Previously, we have studied the structure of 2-(indol-3-yl)-2-(pyridin-3-yl)- and 2-(1-methylbenzimidazol-2-yl)-1-nitroethenes [3, 4]. They are highly conjugated systems existing in the form of *E*-isomer, and their molecules are substantially planar. Ethyl β-nitroacrylate is *E*-configured as well, and the C=C and C=O bonds are in *s-cis* conformation [5].

This work aimed at study of *gem*-substituted nitrostyrenes (ethyl α-nitrocinnamates **I**–**III**) structure by the dipole moments and quantum chemical calculations methods. The structures of *Z*- and *E*-isomers of **I**–**III** are shown below.



X = H (**I**), NMe_2 (**II**), NO_2 (**III**).

We determined the experimental dipole moments of all three compounds in benzene and dioxane solutions (Table 1) and calculated their dipole moments (μ_{calc}) by a vector-additive scheme and quantum-chemical methods (μ_{theor}) (Tables 2–4).

The cardinal part of quantum-chemical calculations (search for possible conformations) was performed by a hybrid DFT B3PW91 method in the 6-31G(d) basis using GAUSSIAN 09 software [6]. The so found energetically most favorable conformations were also computed taking advantage of other methods in order to improve the agreement between calculated and experimental values. Compliance of the found stationary points to energy minima was proved by calculation of the second derivatives; in all cases the eigenvalues of the Hessian matrix were positive.

Tables 2–4 show dipole moments calculated by the vector-additive scheme and the respective theoretical values for *Z*- and *E*-isomers of **I**–**III**, as well as their relative energies. For all the compounds examined, relative energy difference between the individual conformers was below 4–5 kJ mol^{-1}.

According to the results of ^1H NMR, IR spectroscopy, and electron microscopy, compounds **I**–**III** existed in the form of individual *Z*-isomers [7].

In the case of compound **I** the energy difference between *Z*- and *E*-isomers was very low (Table 2). In

Table 1. Coefficients of equations and experimental dipole moments of ethyl α-nitrocinnamates **I**–**III** in benzene and dioxane

Comp. no.	Solvent	α	γ	P_{or}, cm^3	μ, D
I	Benzene	4.165	0.167	166.396	2.84
	Dioxane	4.926	0.345	165.764	2.83
II	Benzene	11.896	0.371	484.647	4.84
	Dioxane	17.144	0.793	708.612	5.86
III	Benzene	6.733	0.084	333.173	4.02
	Dioxane	12.006	0.300	512.239	4.98

the *Z*-isomer, the electron density was delocalized from benzene ring via C=C bond to the accepting carbonyl group (the nitro group was rotated out of the C=C bond plane by 93°). This was consistent with the high exaltation of the calculated dipole moments from the experimental one (Δμ = 1 D). Theoretical and calculated values of the dipole moments were quite close. In that case, the C=C and C=O bonds were *s-cis*-located, being consistent with the general rules of conformational analysis in organic chemistry [8]. In the *E*-isomer, the above-described interaction was not possible as the carbonyl group was perpendicular to the C=C bond.

In contrast to esters **I** and **III**, the compound **II** was chromatic (orange). Since the strong electron-donating substituent (dimethylamino group) and the deficient carbonyl and nitro groups were located in the opposite parts of the conjugated system of **II**, the intramolecular electronic interaction in that molecule was likely quite strong; it was probably further promoted by the benzene ring and the C=C and C=O bonds location in the same plane. In the case of **II**, Δμ was almost 4 D (Table 3), pointing at pronounced transfer of the electron density from the donor part to the acceptor part of the molecule. The nitro group did not participate in the conjugation, as it was rotated out of the C=C bond plane by 66°.

The data for *E*- and *Z*-isomers of α-nitrocinnamate **III** (containing a nitro group in the *para*-position) are given in Table 4. In the cases of both isomers, Δ*E* values were practically identical. As in **III** the electron-accepting groups were located in the opposite parts of the conjugated system, the intramolecular electron donor→acceptor interactions were supposed to be relatively weak as compared those in **II**. Indeed, the experimental dipole moment of the compound **III** *Z*-isomer was in agreement with the respective theoretical as well as additively calculated values.

The experimental dipole moment of the methyl analog of **III** (*Z*-isomer) was of 5.5 D (dioxane) [9]. However, in [9] the preferred *s-trans*-orientation of the C=C and C=O bonds was chosen exclusively by comparing the experimental value with the calculated dipole moments of *s-cis* (5.0 D) and *s-trans* rotamers (5.7 D), being quite close. In the case of the **III** *Z*-isomer (this work), the polarities of *s-cis* (5.19 D) and *s-trans* conformers (6.54 D) were much different, and even the dipole moments data alone allowed choosing the *s-cis* conformation as the preferred one. This was further supported by its lower relative energy (0.19 kJ mol^{-1}), the conformer with *s-trans* orientation of C=C and C=O bonds was of 7.64 kJ mol^{-1} higher in energy.

Table 2. Relative energy and dipole moments (calculated and theoretical) of *E*- and *Z*-isomers of **I**

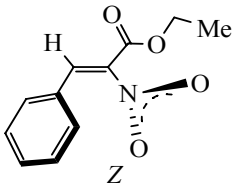
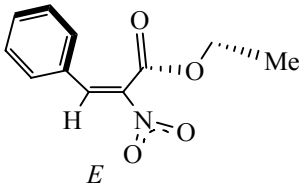
Parameter	 *Z*	 *E*
Δ*E*, kJ mol^{-1}	0.75	0.00
μ_{calc}, D	1.81	2.85
μ_{theor} [B3PW91/6-31G(d)], D	1.76	4.98
μ_{theor} (PM3), D	2.74	4.98
μ_{theor} [HF/6-31G(d)], D	2.26	5.27
μ_{theor} [B3PW91/6-311++G(df,p)], D	1.89	5.46
μ_{theor} [MP2/6-31G(d)], D	2.48	7.24

Table 3. Relative energy and dipole moments (calculated and theoretical) of *E*- and *Z*-isomers of **II**

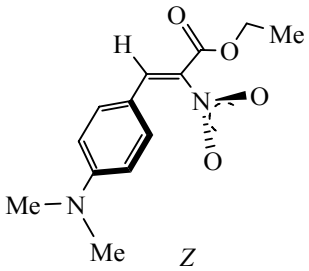
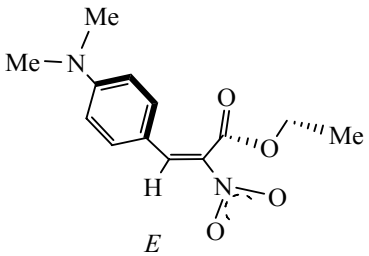
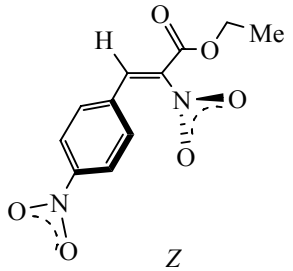
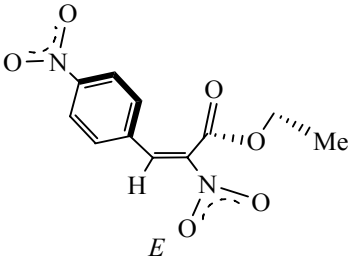
Parameter	 *Z*	 *E*
ΔE, kJ mol^{-1}	2.43	0.00
μ_{calc}, D	1.96	4.15
μ_{theor} [B3PW91/6-31G(d)], D	5.78	9.03
μ_{theor} (PM3), D	4.22	6.49
μ_{theor} [HF/6-31G(d)], D	4.84	8.08
μ_{theor} [B3PW91/6-311++G(df,p)], D	5.79	9.71
μ_{theor} [MP2/6-31G(d)], D	4.65	9.68

Table 4. Relative energy and dipole moments (calculated and theoretical) of *E*- and *Z*-isomers of **III**

Parameter	 *Z*	 *E*
ΔE, kJ mol^{-1}	0.19	0.00
μ_{calc}, D	5.19	2.18
μ_{theor} [B3PW91/6-31G(d)], D	4.92	2.41
μ_{theor} (PM3), D	5.55	1.90
μ_{theor} [HF/6-31G(d)], D	5.43	2.26
μ_{theor} [B3PW91/6-311++G(df,p)], D	5.18	2.43
μ_{theor} [MP2/6-31G(d)], D	5.57	2.07

The preference of *s-cis* conformation in the case of ethyl α-nitrocinnamate **III** was additionally confirmed by X-ray diffraction analysis [10]. In the solid phase, **III** existed in the form of *Z*-isomer, the nitro group being substantially out-of-plane (by 80.5°), and the acrylate moiety was *s-cis*-oriented.

Thus, study of ethyl α-nitrocinnamate structure by combination of dipole moments and quantum-chemical calculations methods revealed that those compounds were *Z*-configured in solution, thus their nitro and aryl substituents were *cis*-oriented.

EXPERIMENTAL

The experimental dipole moments of α-nitrocinnamates **I**–**III** were determined by the second Debye method [11]. The coefficients of equations and the orientational polarization are collected in Table 1. The dielectric constants of **I**–**III** solutions in benzene and dioxane were determined at 25°C with BI-870 instrument (Brookhaven Instruments Corporation) with the accuracy of ±0.01. Refractive indices of the solutions were determined with RA-500 refractometer (Kyoto Electronics) with the accuracy of ±0.0001. The

experimental dipole moments were determined as in Eq. (1).

$$\mu = 0.01283\sqrt{P_{or}T}\times 10^{-18}. \quad (1)$$

Orientation polarization (P_{or}) was determined by the Guggenheim–Smith equation (2) [11].

$$P_{or} = (M/d)\{[3\alpha/(\varepsilon_0 + 2)^2] - [3\gamma/(n_0^2 + 2)^2]\}. \quad (2)$$

In Eq. (2), M is molecular weight of the substance; d is the solvent density; α and γ are the slopes of the linear plots ε_i–w_i and n_i^2–w_i; ε_i, n_i, and w_i are dielectric constant, refractive index and weight fraction of the solute in the i-th solution, respectively.

For the dipole moments calculation via the vector-additive scheme we used the geometric parameters obtained from the quantum-chemical calculations and the following dipole moments of the bonds and groups: m(Ph–C_{sp2}) = 1.07 D (calculated from μ_{exp} of CH_2=CHC_6H_5 [11]), m(H–C_{sp2}) = 0.70 D [12], m(C_{sp2}–NO_2) = 2.81 D (calculated from μ_{exp} of CH_2=$CHNO_2$ [11]), m(C=O) = 1.94 D [13], m(p-$Me_2NC_6H_4$–C_{sp2}) = 2.17 D (calculated from μ_{exp} of p-$Me_2NC_6H_4CH$=CH_2 [11]), m(C_{sp2}–$C_6H_4NO_2$-p) = 3.54 D [14], m(C_{sp2}–O) = 0.18 D (calculated from μ_{exp} of $CH_3C(O)OEt$ [11]), m(Et–O) = 1.1 D (calculated from μ_{exp} of Et_2O [11]).

Compounds **I** and **II** were prepared as described in [7]; compound **III** was obtained as described in [15].

The calculations were performed in the Kazan Branch of the Joint Supercomputer Center of the Russian Academy of Sciences.

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