ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 11, pp. 1562–1564. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © Ya.A. Vereshchagina, A.Z. Alimova, D.V. Chachkov, E.A. Ishmaeva, E.K. Slobodchikova, V.M. Berestovitskaya, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 11, pp. 1578–1580.

Study of the Structure of 1-Nitro-3,3,3-trifluoro– and 1-Nitro-3,3,3-tribromopropenes by the Methods of Dipole Moments and Quantum Chemistry

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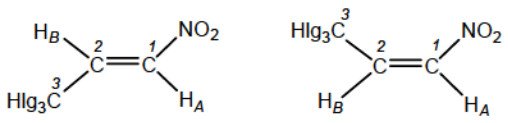
Received July 16, 2014

Abstract—Method of dipole moments and quantum-chemical calculations allowed establishing that 1-nitro-3,3,3-trifluoro– and 1-nitro-3,3,3-tribromopropenes have the *E*-configuration (the nitro group and the trihalomethyl substituent are in the *trans*-position); the obtained characteristics were compared with the corresponding data for the trichloromethyl-containing analog.

DOI: 10.1134/S1070428014110049

Conjugated nitroalkenes with a bulky trihalomethyl group are interesting both from theoretical and practical viewpoint; their practical usefulness is due to the possibility to apply polyhaloalkenes and -alkanes, in particular, as pesticides. The closest analog of the mentioned halonitroalkene, 1-nitro-3,3,3-trichloropropene (**I**) exhibits the fumigant and nematocidal mode of action [1, 2], and the 2-hydroxy-1-nitro-3,3,3-trichloropropane exhibits the herbicidal properties [3]. We formerly investigated the structure of 1-nitro-3,3,3-trichloropropene (**I**) [4] and established that this compound has the *E*-configuration (the nitro– and the trichloromethyl groups are in the *trans*-position with respect to the double C=C bond).

In this study the structure of trifluoromethyl- (**II**) and tribromomethyl- (**III**) nitropropenes was investigated by the methods of dipole moments and quantum chemistry and the results obtained were compared with the data for compound **I**.



E *Z*

I–III

Hlg = Cl (**I**), F (**II**), Br (**III**).

In Table 1 the coefficients of the calculation equations, orientation polarizations, and the experimental dipole moments of nitropropenes **I**–**III** are compiled. Below the *E*– and *Z*-isomers of compound **I**–**III** are presented.

The relative energies, theoretical dipole moments and dipole moments calculated along the vector-additive scheme of the geometric isomers of compounds **I**–**III** are presented in Table 2.

As seen from Table 2, the experimental dipole moment of nitropropene **I** is close to that calculated by the vector-additive scheme for the *E*-isomer. The theo-

Table 1. Coefficients of calculation equations and experimental dipole moments of compounds **I** [4]–**III** in benzene

Compound no.	α	γ	P_{or}, cm^3	μ, D
I	2.561	0.084	88.0742	2.08
II	3.306	–0.416	99.002	2.19
III	2.915	0.131	169.650	2.87

Table 2. Relative energies, theoretical dipole moments and those calculated by the vector-additive scheme for *E*- and *Z*-isomers of compounds **I** [4]–**III**

Compound no.	Isomer	ΔE, kJ mol^{-1}	μ_{theor}, D	μ_{calc}, D	μ_{exp}, D
I	*E*	0.0	2.24	2.25	2.08
	Z	8.8	3.43	4.23	
II	*E*	0.0	1.68	2.23	2.19
	Z	26.1	4.01	4.15	
III	*E*	0.0	3.16	2.86	2.87
	Z	39.1	3.12	3.88	

retical dipole moment of the *E*-isomer [DFT B3LYP/6-31G(d)] sufficiently adequately describes the polarity of compound **I**. The energy minimum also corresponds to this isomer. All combination of the obtained data permits a conclusion that 1-nitro-3,3,3-trichloropropene (**I**) exists in solution as a geometric isomer with the *trans*-position of NO_2 and CCl_3 groups, i.e., compound **I** has the *E*-configuration [4–7].

In the IR spectra of nitropropene **I** in agreement with its structural formula the characteristic bands are clearly seen, ν, cm^{-1}: ~3100 (C–H), ~1660–1620 (C=C), ~1540–1550, ~1320–1360 (NO_2), etc. The calculation confirms and refines these assignments. We succeeded to describe theoretically the experimental vibration spectra based on the theoretical calculations, the limits of the 95% confidence interval are within 4.5–13.8 cm^{-1} [4, 5].

According to the results of the quantum-chemical calculations [DFT B3PW91/6-311++G(df,p)] for compound **II**, the minimum energy also corresponds to the *E*-isomer where the nitro group is located in the plane of the C=C bond, whereas in *Z*-isomer the nitro group is normal to the plane of the C=C bond. *Z*-Isomer possesses relatively large energy (ΔE > 26 kJ mol^{-1}). The theoretical dipole moment of the isomer with the zero energy sufficiently well describes the experimental polarity (Table 1). Therefore compound **II** exists in solution as a geometric isomer with the *trans*-position of NO_2 and CF_3 groups.

In [8] the crystal structure of tribromomethyl derivative **III** was explored. The compound exists in the crystal as a geometric *E*-isomer.

^{1}H NMR spectrum of nitropropene **III** contains two doublets corresponding to vicinal protons H_A (7.36) and H_B (7.76 ppm) with the spin-spin coupling constant $^3J(H_AH_B)$ 12.51 Hz confirming the *E*-configuration of the molecules of this compound. In the IR spectrum of *E*-nitropropene **III** the absorption bands of the conjugated nitro group appear at 1543 and 1347 cm^{-1}, of the double bond C=C, at 1658 cm^{-1} [8].

According to the results of the quantum-chemical calculations [DFT B3PW91/6-311++G(df,p)] for 1-nitro-3,3,3-tribromopropene (**III**), the minimum energy also corresponds to *E*-isomer where the nitro group is located in the plane of the C=C bond. *Z*-Isomer possesses relatively large energy (ΔE > 39 kJ mol^{-1}). The theoretical dipole moment of the isomer with the zero energy sufficiently well describes the experimental polarity. Therefore compound **III** exists in solution as a geometric isomer with the *trans*-position of NO_2 and CBr_3 groups.

Thus irrespective of the nature of the halogen atom in the trihalomethyl group (chlorine, fluorine, bromine) the structure of nitropropenes **I**–**III** in solution is the same: the compounds exist in the *E*-configuration (nitro group and the trihalomethyl substituent are located in the *trans*-position).

EXPERIMENTAL

The polarity of the molecules of substituted nitropropenes **I**–**III** was evaluated by experimental determination of their dipole moments by the second Debye menthod [9]. Coefficients of calculation equations and orientation polarizations are listed in Table 1.

The dielectric permittivity of solutions of compounds **II** and **III** was measured in benzene at 25°C on an instrument BI-870 (Brookhaven Instruments Corporation), accuracy ±0.01. The refraction indices of the solutions were measured on a refractometer RA-500 (Kyoto Electronics), accuracy ±0.0001. The

experimental dipole moment μ was calculated by the formula given below.

$$m = 0.01283\sqrt{P_{or}\,T}.$$

The orientation polarization (P_{or}) is calculated by the Guggenheim–Smith formula [9]:

$$P_{or} = \frac{M}{d}\left[\frac{3\alpha}{(\varepsilon_0 + 2)^2} - \frac{3\gamma}{(n_0^2 + 2)^2}\right],$$

where M is the molecular mass of the compound, d is the density of the solvent, α and γ are slopes of the straight lines ε_i–w_i and n_i^2–w_i; ε_i, n_i, and w_i are dielectric permittivity, refraction index, and the weight fraction of the solute in the ith solution respectively.

In the calculation of dipole moments by the vector-additive scheme we used the values of bond angles obtained from X-ray diffraction analysis [8] and quantum-chemical calculations, and also the following dipole moments of bonds and groups: m (C_{sp^2}→NO_2) 2.81 D, calculated from μ_{exp} CH_2=$CHNO_2$ [9]; m (C_{sp^3}→C_{sp^2}) 0.78 D, calculated from μ_{exp} CH_2=$CHCH_3$ [9]; m(CF_3) 1.36 D, calculated from μ_{exp} CHF_3 [9], m (CCl_3) 1.26 D, calculated from μ_{exp} 1,1,1-trichloroethane [9]; m(CBr_3) 0.73 D, calculated from μ_{exp} $CHBr_3$ [9]; m(H→C_{sp^2}) 0.7 D [10].

Quantum-chemical calculations were carried out applying GAUSSIAN 09 software [11] with a complete geometry optimization. The correspondence of the found stationary points to the energy minima in all instances was proved by the calculation of the second derivative. The calculations were performed in the Kazan Branch of Joint Supercomputer Center of the Russian Academy of Sciences (http://wt.knc.ru).

The syntheses of 3,3,3-trichloro- (**I**) [12], 3,3,3-trifluoro- (**II**) [13, 14], and 3,3,3-tribromo-1-nitropropenes (**III**) [8] were carried out along the indicated procedures. 1-Nitro-3,3,3-trifluoropropene (**II**) is a strong lacrimator.

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