INVESTIGATION OF THE ELECTRON STRUCTURES OF 2-SUBSTITUTED 1,3-DIOXANES BY THE METHOD OF MODIFIED NEGLECT OF DIFFERENTIAL OVERLAP (MNDO)

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UDC 547.841:539.193

The three-dimensional and electron structures of 2-substituted 1,3-dioxanes were investigated by the SCF MO LCAO method within the MNDO approximation. Satisfactory agreement between the calculated and experimental geometrical and energy parameters was obtained. The highest occupied molecular orbital (HOMO) of 2-methyl-, 2-trichloromethyl-, 2-trifluoromethyl-, and 2,2-bis(chloromethyl)-1,3-dioxanes has A' symmetry. The results of the calculations were compared with data from electron-diffraction studies and the photoelectronic spectra.

Cyclic acetals find extensive application and show promise for use in various areas of the national economy [1]. Rather comprehensive experimental data that describe their structures and spectral properties have been accumulated, whereas data on the electron structures of substituted 1,3-dioxanes are scarce and contradictory.

Within the framework of the method of modified neglect of differential overlap (MNDO) [2] we calculated 1,3-dioxane and 2-methyl-, 2-trichloromethyl-, 2-trifluoromethyl-, and 2,2-bis(chloromethyl)-1,3-dioxanes (I-V). Optimization of the geometrical parameters was carried out for all of the molecules (Tables 1 and 2).

The bond lengths in the I molecule are in satisfactory agreement with the experimental values within the range of the error in the determination. The agreement for the bond and dihedral angles is somewhat poorer: a more planar configuration of the aliphatic part of the ring was obtained in the calculations.

The energy of the highest occupied molecular orbital (HOMO) of 1,3-dioxane is −10.97 eV, which is in quite good agreement with the experimental value of the ionization potential (10.10 eV). The disposition of the other energy levels correlates well with the experimentally observed ionization energies (Fig. 1). Thus the MNDO method, in contrast to the CNDO/2 method [4], reproduces both the geometrical characteristics and the ionization potentials in 1,3-dioxane: this makes it possible for one to hope for a rather accurate reproduction of these parameters in compounds that are related to it.

The calculation of all of the monosubstituted 1,3-dioxanes was carried out for two possible orientations of the substituent. A conformation with an equatorial orientation of the substituent is the primary one for II. The difference in the heats of formation of the axial and equatorial conformers is 16.7 kJ/mole, which is in good agreement with the ΔH_{ae} value obtained experimentally from measurement of the appearance potentials of $[M - CH_3]^+$ ions in the mass spectrum of 2-methyl-1,3-dioxane (15.9 ± 1.1 kJ/mole) [5].

The geometrical parameters of the rings of 1,3-dioxanes II-IV, which have substituents with different natures in an equatorial orientation at the $C_{(2)}$ atom, differ insignificantly from the corresponding geometrical parameters of unsubstituted 1,3-dioxane (Table 2). Replacement of a hydrogen atom by a methyl group leads to slight crimping of the acetal part of the ring with respect to dioxane I, while the introduction of the strong CF_3 acceptor group entails a certain degree of flattening of the ring. The introduction of substituents with both electron-donor and electron-acceptor character into the axial conformation leads to flattening of the ring, which is greater, the more bulky the substituent. In the case of the trichloromethyl derivative the minimum for the axial conformation of the substituent cannot be localized within the framework of the Fletcher—Powell optimization procedure. Optimization of angles α and β leads to localization of the equatorial form.

Ufa Petroleum Institute, Ufa 450062. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 894-897, July, 1987. Original article submitted January 27, 1986.

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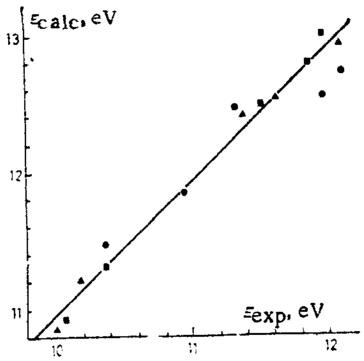

Fig. 1

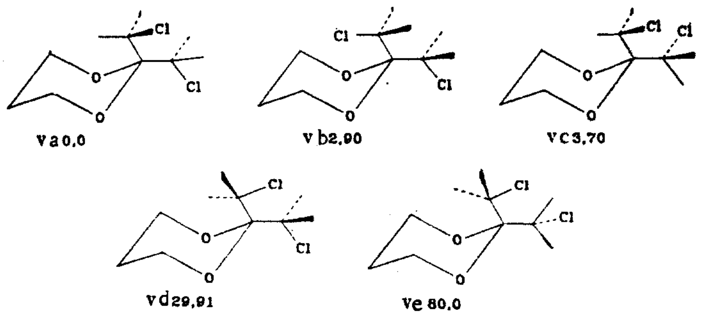

Fig. 2

Fig. 1. Correlation diagram of the calculated and experimental values of the ionization energies: Solid square) I; solid triangle) II; solid circle) III.

Fig. 2. Relative conformational energies (kJ/mole) for several possible conformations of the V molecule.

TABLE 1. Geometrical Parameters of 1,3-Dioxane

Bond angles	Calc.	Exptl. [3]	Bond lengths	Calc.	Exptl. [3]	Diheral angles*	Calc.	Exptl. [3]
$O—C—O_{(3)}$	110,5	115±2,5	$O_{(1)}—C_{(2)}$	1,41	1,393±0,025	α	137,5	132±2,5
$C_{(2)}—O_{(3)}—C_{(4)}$	119,9	110,9±1,5	$O_{(3)}—C_{(4)}$	1,41	1,44±0,04	β	147,12	124±2,5
$O_{(3)}—C_{(4)}—C_{(5)}$	112,5	109,3±1,5	$C_{(4)}—C_{(5)}$	1,56	1,53±0,015			
C—C—C	112,5	107,7±1,1						

*Angles α and β are the angles between the "chair-seat" planes and the acetal and aliphatic fragments, respectively.

TABLE 2. Optimal Values of the Geometrical Parameters of Monosubstituted 1,3-Dioxanes

Geometrical parameters *	I	II		III		IV (eq)
		eq	ax	eq	ax	
Bond lengths, Å						
$O_{(1)}—C_{(2)}$	1,41	1,41	1,41*	1,405	1,405	1,405
$O_{(3)}—C_{(4)}$	1,41	1,41	1,41*	1,41	1,41	1,41
$C_{(4)}—C_{(5)}$	1,56	1,56	1,56*	1,56	1,56	1,57
$C_{(2)}—C_{(7)}$	—	1,56	1,56*	1,62	1,65	1,58
C—Cl	—	—	—	—	—	1,79
C—F	—	—	—	1,35	1,35	—
Bond angles, deg						
$O_{(1)}—C_{(2)}—O_{(3)}$	110,5	109,6	109,6*	111,7	110,5	110,5
$C_{(2)}—O_{(3)}—C_{(4)}$	119,9	119,5	124,6	120,6	127,1	120,2
$C_{(2)}—C_{(7)}—Cl$	—	—	—	—	—	111,5
C—C—F	—	—	—	112,0	112,4	—
Dihedral angles, deg						
α	137,5	135,7	147,8	140,2	156,9	138,0
β	147,1	147,2	147,2*	147,1	149,0	147,5

*The bond lengths and bond angles were taken from calculations of the equatorial conformer.

For V we examined various conformations of the chloromethyl groups (Fig. 2). Structure Va is the primary structure. For 2,2-bis(chloromethyl)-1,3-dioxane we optimized only the values of angles α and β; in the primary conformation they are 151.3 and 149.1°, respectively.

An analysis of the composition of the molecular orbitals shows that the nature of the HOMO remains constant for all of the investigated compounds. The HOMO is formed primarily by a symmetrical combination of the 2p orbitals of the oxygen atoms (A' type symmetry). As a consequence of this, the axial position at one of the oxygen atoms of the 1,3-dioxane molecule

TABLE 3. Charges on the Atoms of the Investigated Compounds

Atom	I	II		III		IV
		eq	ax	eq	ax	
$O_{(1)}$	−0,37	−0,36	−0,39	−0,35	−0,38	−0,35
$C_{(2)}$	0,34	0,29	0,32	0,31	0,37	0,33
$O_{(3)}$	−0,37	−0,36	−0,39	−0,35	−0,38	−0,35
$C_{(4)}$	0,18	0,18	0,20	0,18	0,21	0,18
$C_{(5)}$	−0,09	−0,09	−0,10	−0,09	−0,10	−0,10
$C_{(6)}$	0,18	0,18	0,20	0,18	0,21	0,18
$C_{(7)}$	—	0,05	−0,02	0,60	0,52	0,24
$X_{(1)}$*	—	—	—	−0,21	−0,23	−0,10
$X_{(2)}$	—	—	—	−0,22	−0,23	−0,10
$X_{(3)}$	—	—	—	−0,22	−0,23	−0,10

*Atom X = F, Cl.

is the most likely direction of attack by an electrophilic particle. The introduction of an electron-donor substituent into the equatorial position leads to an increase in the energy of the HOMO, while the effect of an electron-acceptor substituent is opposite in character. This is responsible for the corresponding increase and decrease in the reactivities of substituted 1,3-dioxanes in acid-catalyzed reactions. A comparison of the calculated energies of the MO of equatorially substituted structures with the experimentally measured ionization potentials provides evidence for the rather good correlation between these values (Fig. 1).

The basicities of 1,3-dioxanes in most cases are determined by the magnitudes of the charges on the oxygen atoms [6]. The electron distribution that we obtained shows that even the introduction of a substituent with strongly expressed electron-acceptor properties changes the charges on the oxygen atoms only slightly (Table 3). A certain increase in the charges on the oxygen atoms is characteristic for molecules with an equatorial orientation of the substituents. The charge on the $C_{(2)}$ atom is most sensitive to the introduction of a substituent.

Thus our investigations provide evidence that the MNDO method satisfactorily reproduces the geometrical parameters and ionization energies of the investigated compounds; the introduction of a substituent into the axial position at the $C_{(2)}$ atom leads to a greater change in the geometry of the heteroring and the energy of the HOMO than substitution of an equatorial hydrogen atom; as in 1,3-dioxane, the HOMO in 2-substituted 1,3-dioxanes has A' symmetry.

EXPERIMENTAL

The calculations were made from the MNDO program, which realizes the algorithm of the MNDO method with optimization of the geometry in accordance with the Fletcher–Powell method. The program was adapted for EC and CYBER-170 computers.

The authors thank co-workers of Tratu University N. V. Villem and Ya. Ya. Villem for recording the photoelectronic spectra.

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