Computation of conformations of 2-(2-hydroxyethoxy)-3,4-dihydropyran with intramolecular hydrogen bonds

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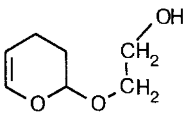
The conformations of 2-(2-hydroxyethoxy)-3,4-dihydropyran were calculated by the methods of molecular mechanics and MNDO/H with and without allowance for the formation of intramolecular hydrogen bonds. Two possible centers of the formation of the intramolecular hydrogen bond, *viz.*, the oxygen atoms of the alkoxy radical and of the dihydropyran cycle, have been considered. The results obtained show that 2-(2-hydroxyethoxy)-3,4-dihydropyran does not exist in any preferable conformation.

Key words: hydrogen bond; MNDO; 2-(2-hydroxyethoxy)-3,4-dihydropyran.

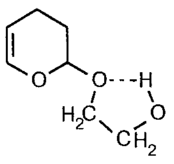
The earliest spectral studies of hydroxyl-containing vinyl ethers showed that these compounds form intramolecular hydrogen bonds and exist in the pure state mainly as associates.[1—3] The role of the hydroxyvinyl group in the formation of intramolecular H-bonds remained unlear. In the extensive spectral studies performed later,[4—7] intermolecular interactions[6] under the conditions of high dilution were almost ruled out. The results obtained unambiguously indicated that intramolecular H-bonds existed in the compounds considered, however, the question about the conformations of the H-bonded structures and the forms of participation of the vinyloxy group in them remained unsolved. A theoretical study of the conformers with intramolecular H-bonds may help clarify this problem.

Of several compounds containing hydroxy and vinyloxy groups, 2-(2-hydroxyethoxy)-3,4-dihydropyran (**1**) was chosen as the object for investigations. This compound contains three competing centers prone to formation of an intramolecular H-bond: two oxygen atoms and the multiple bond. The doublet band of the bound hydroxyl in the IR spectrum* (CCl_4, νOH/cm^{-1}: 3615, 3530) of dihydropyran indicates that there exist only two types of intramolecular H-bonds. An analogous doublet (CCl_4, νOH/cm^{-1}: 3614, 3455) of 2-(2-hydroxyethoxy)tetrahydropyran (hydrogenated analog of **1**) convincingly demonstrates the absence in **1** of an intramolecular H-bond with the C=C bond of the dihydropyran cycle.

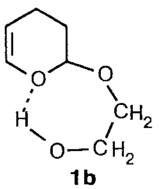
Therefore, we considered two possibilities of the formation of the intramolecular H-bond realized in conformers (**1a** and **1b**).



1



1a



1b

The heat of formation, strain energy, and dipole moment were determined for **1**, **1a**, and **1b** by molecular mechanics.

	1	**1a**	**1b**
ΔH_f^0 /kcal mol^{-1}	−117.9	−120.4	−120.0
E_s /kcal mol^{-1}	−3.3	−5.8	−5.4
μ/D	2.6	2.0	1.9

All of the three conformers may be considered to be almost equally stable within the known error of the calculations, although **1a** is somewhat distinguished in its stability. The dipole moment of **1** is greater because **1** is more extended than **1a** or **1b.**

The MNDO method has recently received wide acceptance[8,9] and it was chosen as the most suitable method for the quantum-chemical calculations of the objects under consideration. A special procedure is used for H-bonds in this method. If the energy of the Coulomb repulsion of the atomic frameworks of A and B (nuclei and electrons of the internal shells) is usually calculated by the formulas:

$$E_{AB} = Z_A Z_B(S^A S^A,\ S^B S^B)(1 + f_3(R_{AB})), \tag{1}$$

$$f_3(R_{AB}) = \exp(-\alpha_A R_{AB}) + \exp(-\alpha_B R_{AB}), \tag{2}$$

where Z_A and Z_B are the charges of the atomic frame-

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* IR spectra in the range of OH stretching vibrations (3660—3400 cm^{-1}) were recorded on a UR-20 spectrometer at concentrations of 0.001—0.002 *M*, which almost excluded intermolecular association. The thickness of the absorbing layer varied from 1.0 to 50 mm.

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works, (S^AS^A, S^BS^B) is the integral of the Coulomb interaction of the electrons located at the valent s-AO of the atoms A and B, and R_{AB} is the interatomic distance, then for H-bonds it is accepted that:

$$f_3(R_{XH}) = R_{XH}\exp(-\alpha_X R_{XH}) + \exp(-\alpha_H R_{XH}). \qquad (3)$$

Here X = N, O, and α_A, α_B, α_X, and α_H are empirical parameters of the corresponding atoms.

Unfortunately, this method of account of the specificity of H-bonds often does not allow one to adequately compensate for the disadvantages of the MNDO method, which are connected with the overestimation of the Coulomb attraction of electrons to atomic nuclei, and therefore, this method does not always result in even qualitative accordance with the experiment.[8,10] It is clear that a more suitable f_3 function could considerably improve the results of the calculation of H-bonds by the MNDO method. In our opinion, of the three tested functions,[10] the following agrees best with the experiment:

$$f_3^H(R_{XH}) = \exp(-\alpha_{XH}R^2_{XH}). \qquad (4)$$

As in the previous calculations,[10] the value α_{XH} was taken to be equal to 2.0 Å^{-2} in all of the calculations using this function. The results of these calculations showed that conformer **1a** is somewhat more stable than **1** or **1b**, although the heats of formation are approximately equal.

	1	**1a**	**1b**
ΔH_f^0 /kcal mol^{-1}	−121.3	−121.5	−120.2

Since **1a** and **1b** have different types of intramolecular H-bonds, it would appear that the H-bond is somewhat more efficient in **1a**. However, this conclusion is premature. The length of the H-bond $l_{O...H}$ in **1b** calculated by the MNDO method is somewhat smaller than that in **1a**, and hence, the bond must be stronger in **1b**.

The partial charges q_i in conformers **1**—**1b** (see below) show that the formation of the intramolecular H-bond results in noticeable changes in the electron populations both of the oxygen atom that participates in this bond, O_R, of the alkoxy radical in **1a** or O_{cycl} of the dihydropyran cycle in **1b**, and of the other atoms. In **1a** and **1b**, not only the H-bonds but also all the other bonds including the multiple bond, are variously polarized. The degree of polarization of the latter is inversely related to the stability of the hydrogen bond formed (compare $\Delta q = \Delta q_{C_2}{}^{C=C} - q_{C_1}{}^{C=C}$ for **1a** and **1b**).

	$q_{C_1}{}^{C=C}$	$q_{C_2}{}^{C=C}$	Δq	$q_{O_{cycl}}$	q_{O_R}	q_H	$l_{O...H}$/Å
1	−0.214	0.117	0.331	−0.306	−0.351	0.184	—
1a	−0.224	0.112	0.336	−0.312	−0.354	0.187	2.62
1b	−0.231	0.113	0.344	−0.328	−0.345	0.196	2.15

Thus, the results of the calculations performed attest to the energetic similarity of conformations **1**—**1b** of the 2-(2-hydroxyethoxy)-3,4-dihydropyran molecule. The preference of conformer **1a** over **1b** cannot be caused by the type of intramolecular H-bond formed, because it is stronger in **1b**. The conclusions drawn confirm many of the suppositions advanced in the experimental study.[4—7]

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