Chemistry of Heterocyclic Compounds, Vol. 44, No. 5, 2008

LETTERS TO THE EDITOR

CONFORMATIONAL ANALYSIS OF TETRAHYDROFURAN AND TETRAHYDROTHIOPENE USING ^{1}H NMR SPECTROSCOPY AND *ab initio* CALCULATIONS

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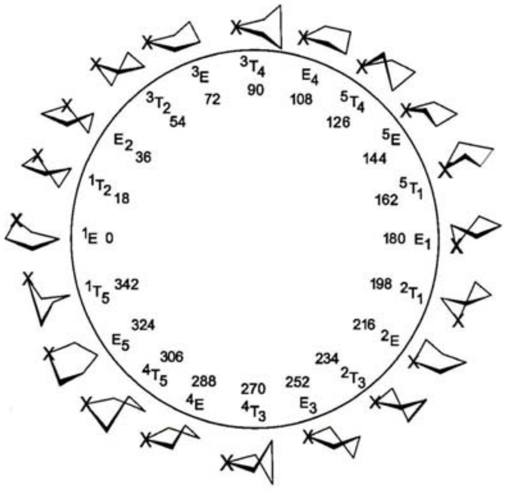
Keywords: tetrahydrothiophene, tetrahydrofuran, conformational analysis.

Coupling constants provide important information on the conformation of molecules in solution. At present, four of the ten possible coupling constants $^nJ_{HH}$ have been experimentally determined for tetrahydrofuran (THF) and tetrahydrothiophene (THT) [1]. We have used these data to evaluate the parameters of the dynamic structure of the THF and TTF molecules in a new scheme for conformational analysis involving the quantum-chemical description of the dynamic systems in terms of large-amplitude oscillations.



X = O, S

Fig. 1. Conformational space of THF and THT.

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Our proposed conformational analysis scheme entails a number of steps. In the initial step, we calculate the potential and coordinates of the reaction pathway for the THF and THT molecules by Hartree-Fok scanning with the 6-311++g** basis functions [2]. The molecular structure of the points on the reaction pathway coordinate was characterized by folding parameters, namely, the pseudorotation phase angle and folding amplitude [3]. The ${}^4T_5$ and ${}^5T_4$ *twist* conformations characterized by the least repulsion of protons of adjacent CH_2 groups correspond to the minimal energy points. The ${}^1E$ and E_1 *envelope* conformations correspond to the transition states (see Figure 1).

In the second step, we calculated the vibrational energy levels and wave functions for pseudorotation carried out by a numerical solution of the one-dimensional Schroedinger equation using the Ritz variational method [4]. The values for the distribution function permitted us to evaluate the coupling constants averaged over thermal motions for each point on the reaction pathway coordinate. Subsequent analysis of the occupancy of the vibrational levels permitted us to calculate the coupling constants for a given temperature.

In the final step, we solved the inverse structural problem with refinement of the potential parameters according to the criterion of best fit of the calculated and experimental coupling constants (see Table 1). Along with the extremely low-energy pseudorotation, THF undergoes ring inversion, thereby converting, for example, from the ${}^3T_4$ form directly to the ${}^4T_3$ form also with a rather low barrier. According to Wu and Cremer [5], this barrier is about 4.5 kcal/mole. These concurrent processes lead to ${}^1H$ NMR spectra in the experiment at room temperature described by $[A]_4[X]_4$ spin systems in accord with the effective C_{2v} molecular symmetry. The coupling constants calculated by Wu [5] without using a dynamic approach are also given for comparison in Table 1. The good accord of our calculated coupling constants with the experimental values supports the conclusions drawn for the structure of the molecules studied.

Minimal folding [3] corresponds to the maximum energy for the THF molecule [3], while the opposite behavior is observed for THT. The folding upon displacement along the reaction pathway coordinate varies from 0.35 to 0.38 Å for THF and from 0.43 to 0.49 Å for THT. In our opinion, this behavior should be attributed to the significant differences in the structures of these molecules. The THF molecule can be obtained formally by replacing a CH_2 group in cyclopentane by an oxygen atom, which is similar in size and mass. This replacement leads only to a slight change in the molecular skeleton, making it slightly more planar, while the analogous replacement of a CH_2 group by a sulfur atom markedly alters the total structure. In particular, the C–X–C valence angle is compressed from 108.5° in cyclopentane [5] to ~94° in THT. The molecule becomes much more folded, as confirmed by our calculations. The introduction of a heavy sulfur atom markedly extends the overall reaction pathway, which is 23.04 $V\cdot(\mathrm{amu})^{0.5}$ for THF. The overall reaction pathway is 31.107 $V\cdot(\mathrm{amu})^{0.5}$ for THT.

This work was carried out with the support of the Russian Fundamental Research Fund (Grant No. 06-03-32800).

TABLE 1. Comparison of Calculated and Experimental Coupling Constants (Hz) for THF and THT

Coupling constant type	Tetrahydrofuran			Tetrahydrothiophene	
	Present work	Calculation [5]	Experiment [1]	Present work	Experiment [1]
${}^3J^{trans}_{2,3}$	5.93	5.35	6.14	6.02	6.66
${}^3J^{cis}_{2,3}$	8.19	7.33	7.94	7.25	6.66
${}^3J^{trans}_{3,4}$	6.26	5.50	6.25	7.43	7.35
${}^3J^{cis}_{3,4}$	8.56	8.51	8.65	5.46	5.5

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