



Two-dimensional character of internal rotation of furfural and other five-member heterocyclic aromatic aldehydes



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ABSTRACT

The features of nuclear motion corresponding to the rotation of the formyl group (CHO) are studied for the molecules of furfural and some other five-member heterocyclic aromatic aldehydes by the use of MP2/6-311G** quantum chemical approximation. It is demonstrated that the traditional one-dimensional models of internal rotation for the molecules studied have only limited applicability. The reason is the strong kinematic interaction of the rotation of the CHO group and out-of-plane CHO deformation that is realized for the molecules under consideration. The computational procedure based on the two-dimensional approximation is considered for low lying vibrational states as more adequate to the problem.

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1. Introduction

The potential functions of internal rotation of the molecules are the traditional results of conformational analysis representing in a compact form a large part of the spectroscopic data. These functions are used for calculations of the properties of the molecules and substances, for analysis and forecast of the physical and chemical processes associated with internal rotation and other.

There exist a number of different approaches to construct potential functions of internal rotation. Within one of the most widely used models, the internal rotation is considered as the one-dimensional (1D) motion of nuclei, which does not directly depend on other intramolecular motions.

For a number of molecular systems the approximations of this type are quite reliable. But it is possible to find the other situations, where the attempts to reduce the multidimensional potential energy surface (PES) to the 1D potential function of internal rotation lead to catastrophes, bifurcations and hysteretic loops [1]. Another example of unreliability of 1D approximation is the very strong coupling of two internal rotations (symmetrical and asymmetrical) in *cis* conformer of methyl cyclopropyl ketone ($c\text{-C}_3\text{H}_5\text{COCH}_3$) [2]. This is the case when a part of the minimal energy path between two conformers cannot be considered in approximation of separated vibrations.

For a long time there were known the molecular systems where was found essential discrepancy of theoretical and experimental estimates for potential barriers defined in 1D approximation. Recently, at least one

possible reason of such problems was described: the non-trivial situation of significant kinematic (but not dynamic) interaction between torsional vibration and out-of-plane CHO deformation for benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) [3]. Taking into account this kinematic interaction one may find the good agreement between experimental and calculated energies of torsional and out-of-plane CHO deformation energy levels in the frame of the two-dimensional (2D) approximation for the vibrational problem, while differences within the usual one-dimensional (1D) approximations are essential. In contrast to the benzaldehyde molecule, the 1D potential function of internal rotation for related molecule of benzoyl fluoride ($\text{C}_6\text{H}_5\text{CFO}$) calculated as the minimal energy path is quite reliable; as a result, the 1D and 2D energies of the torsional energy levels are practically the same. This example and the results of testing of the similar molecules Ph-CXY demonstrate clearly that one may expect the significant kinematic interaction between torsional vibration and out-of-plane CXY deformation for the systems where the masses of atoms X and Y differ essentially, as it is in the benzaldehyde molecule, but not in the benzoyl fluoride molecule [3].

The situation described seems to be interesting for the vibrational theory of molecular systems. That is why in the paper presented the possibility of analogous effects is analyzed in the case of the molecules formed by the substituted aromatic rings differed from the benzene ring. The molecules of the 2- and 3-formyl-derivatives of the furan or the similar systems with other heteroatom (S, Se, and Te) (see Fig. 1) were chosen with aromatic fragments of essentially lower symmetry than in one-substituted benzenes.

Among the molecules mentioned there is only one system well studied by vibrational spectroscopy. Both from the experimental studies [4,5] and quantum-chemical calculations (see for example [6]) it is known that

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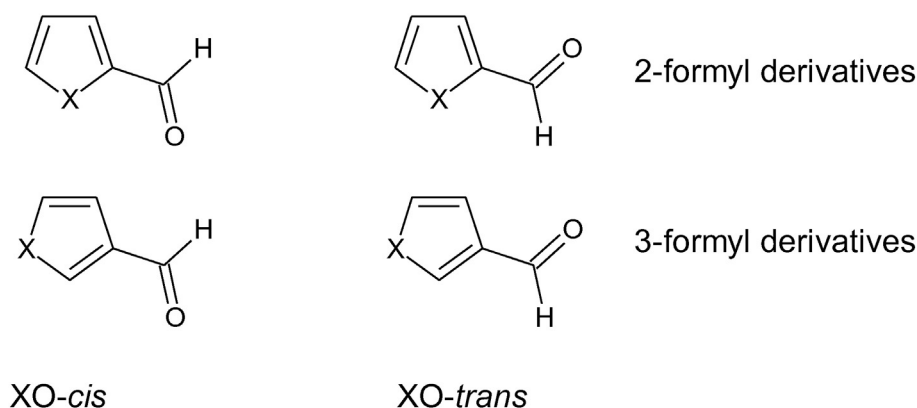


Fig. 1. XO-*cis* and XO-*trans* conformers of formyl derivatives of furan, thiophene, selenophene and tellurophene. Below, the following notations for substances are used: X = O – furfural and 3-formyl furan, X = S – 2- and 3-formyl thiophene, X = Se – 2- and 3-formyl selenophene, X = Te – 2- and 3-formyl tellurophene.

the furfural molecule (2-furaldehyde, that is, 2-formyl furan) exists as a pair of plane conformers (C_s point symmetry group), namely OO-*cis* and OO-*trans* (the simplified notations *cis* and *trans* for corresponding conformers are used below, see Fig. 1). Eight torsional transition energies were experimentally found for the conformers of furfural molecule in work [4]. Hence, one can hope to determine the potential function of internal rotation of high accuracy.

2. Computational details

The study of the problems above described was realized in two stages. First of all the electronic energies of the molecules under consideration were calculated by the *ab initio* quantum chemistry methods. Optimization of total energy defined the geometry parameters of equilibrium configuration. The vibrational frequencies were estimated within the traditional harmonic approximation.

For quantum chemical analysis of the electron problem and PES estimations for molecules containing O and S in ring the main approximation was used for the type MP2/6-311(*d,p*). The same approximation was quite adequate in the case of benzaldehyde molecule [3]. The calculations of molecules with oxygen substituted by Se or Te atoms were carried out with correlation-consistent polarized valence triple-zeta basis set (cc-pVTZ) for C, O, and H. For Se and Te, the small-core relativistic effective core potentials [7] of the Stuttgart/Köln group ECP10MDF and ECP28MDF, respectively, with the associated cc-pVTZ basis sets to describe the valence electrons were employed.

All the *ab initio* calculations were performed by the MOLPRO 2010.1 quantum-chemistry program package [8].

Just as for the benzaldehyde [3], the low-lying vibrational states could correspond to the motions of the complex form that may be approximately described as internal rotation of the molecule accomplished by the motion of the formyl group out of the plane of the aromatic ring. That is why at the second stage of calculations for the two interacting modes of the symmetry type A'' (denoted here approximately as torsional vibration and out-of-plane CHO deformation) the 1D and 2D vibrational problems were solved on the basis of quantum chemical PES calculations.

The vibrational coordinates of internal rotations τ and out-of-plane vibration of the formyl group χ were defined here by the use of the dummy atoms A_1 and A_2 (see Fig. 2). Here and below the same symbolic notations are used for both vibrational coordinates τ and χ and corresponding vibrational motions. Both the segments of straight lines A_1C_2 and A_2C_6 are orthogonal to the bond C_2C_6 . The point A_1 belongs to the plane (XC_2C_3) of the aromatic ring, while the point A_2 belongs to the plane $H_8C_6O_7$ of the carbonyl group. The internal rotation coordinate τ is defined as the dihedral angle $\angle A_1C_2C_6A_2$. The coordinate χ for out-of-plane CHO deformational vibration is the angle of the bond C_2C_6

with the plane XC_2C_3 for 2-formyl derivatives and $C_1C_2C_3$ for 3-formyl derivatives.

The 1D or/and 2D cross-sections of PES were constructed on the basis of the system of reference points in the region defined by conditions $0 \leq \tau \leq 180^\circ$ and $-25^\circ \leq \chi \leq 25^\circ$. For reference points, the steps 15° for τ and 5° for χ were used (one may evaluate the energy values in a small number of the points due to the symmetry of the problem). The other geometrical parameters of the nuclear configuration were defined by minimization of the total electronic energy for each reference point (the values of τ and/or χ coordinates). It is worth to note that the region of the relatively large values of the coordinate χ may be ignored, as the potential energy in this region is too large due to the essential steric strain: the energy levels are insensitive to the variations of wave functions in such regions, because the nuclear density is too small to have any influence on the intramolecular forces.

For the vibrational Schrödinger equations were solved numerically by the computer programs TORSIO [9] and Vib2D [10] realizing the algorithm similar to that described by Lewis et al. [11] for the states with zero nuclear angular momentum. The 1D vibrational states were calculated by the Rayleigh–Ritz method in the basis of trigonometrical basic functions for the Hamiltonian of the form

$$H_{1D} = -\frac{\partial}{\partial \varphi} B(\varphi) \frac{\partial}{\partial \varphi} + V(\varphi) \quad (1)$$

where $\varphi = \tau$ or χ . Here $B(\varphi)$ is the kinematic function expressed by the trigonometric decomposition of the form

$$B(\varphi) = B_0 + \sum_n B_n \cos(n\varphi). \quad (2)$$

For the potential function $V(\varphi)$ the traditional form is used:

$$V(\varphi) = \frac{1}{2} \sum_n V_n (1 - \cos(n\varphi)). \quad (3)$$

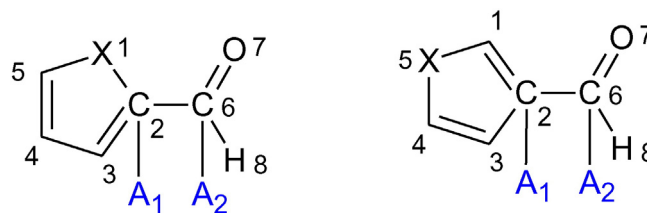


Fig. 2. The atom numbering in the molecules under investigation. X = O, S, Se, Te. The dummy atoms A_1 and A_2 used to set the internal rotation coordinate are also depicted (see the text).

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