DENSITY FUNCTIONAL THEORY STUDY OF THE ROTATIONAL BARRIERS, CONFORMATIONAL PREFERENCE, AND VIBRATIONAL SPECTRA OF 2-FORMYLFURAN AND 3-FORMYLFURAN

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The torsional potentials, molecular structures, conformational stability, and vibrational wavenumbers for the rotational isomers of 2-formylfuran and 3-formylfuran are computed using the density functional theory (B3LYP) method with the 6-31+G* basis set. All structures are fully optimized and the optimized geometries, rotational constants, dipole moments, and energies are presented. From the computations, both 2-formylfuran and 3-formylfuran are predicted to exist predominantly in *trans* conformation with a *cis—trans* rotational barrier of 11.19 kcal/mol and 8.10 kcal/mol, respectively. The vibrational wavenumbers and the corresponding vibrational assignments of the molecules in the C_s symmetry are examined and the infrared spectra of the molecules are simulated using the wavenumbers and the corresponding intensities obtained from the computations. The effect of solvents on the conformational stability of all the molecules in nine different solvents (heptane, chloroform, tetrahydrofuran, dichloroethane, acetone, ethanol, methanol, dimethylsulfoxide, and water) is investigated. The integral equation formalism in the polarizable continuum model (IEF-PCM) is used for all solution phase computations.

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K e y w o r d s: density functional theory, rotational barrier, vibrational wavenumber, conformational preference, infrared spectra, geometry optimization, solvent effect, formylfuran, furan carbaxaldehyde, polarizable continuum model.

INTRODUCTION

The 2-formylfuran and 3-formylfuran molecules, which are also known as 2-furan carboxaldehyde (furfural) and 3-furan carboxaldehyde respectively, are furan derivatives with the chemical formula C_4H_3OCHO. These molecules contain an aldehyde (—CHO) group substituted at positions 2 and 3 by the oxygen atom of a furan ring. Infrared and Raman spectra of 2-formylfuran were first studied by Allen and Bernstein [1]. Since then, numbers of experimental and theoretical studies [2—15] have dealt with the infrared, Raman, and microwave spectra of the 2- and 3-subtituted derivatives. Allen and Bernstein [1] reported that these compounds exist as an equilibrium mixture of two rotational isomers (OO-*trans* and OO-*cis*). Karabatsos and Vane [2] reported NMR studies of the long-range spin-spin coupling constants between the aldehydic and the aromatic protons in solution and concluded that 2-formylfuran exists in OO-*cis*, while OO-*trans* was found to be favored in the gas phase far-infrared and Raman spectroscopic analysis [6]. Motiyenko et al. [10] reported a microwave spectroscopy study of 2-formylfuran in vibrational excited states and concluded that the *cis* conformer

is less stable than the *trans* conformer by 286 cm^{-1}. The effect of conformation on the force field and vibrational spectrum of 2-formylfuran were reported using CNDO/2 force field calculations [5]. John et al. [14] reported the *ab initio* molecular calculation for the study of 2-formylfuran, 3-formylfuran, and other related molecules and they found that the *cis-trans* forms of 3-formylfuran are virtually equi-energetic in the gas phase, while the *trans* conformer of 2-formylfuran is energetically favored by 3.5 kJ/mol. In general, the small energy difference between the two rotational conformers of 2-formylfuran and its strong solvent dependence make unambiguous assignments of the experimental spectral results difficult [7]. Thus, the ability to reliably predict the conformational preference and the rotational barrier is of great interest for systems where the experimental conformational preference is not clear and is strongly solvent dependent. This brief review of the literature shows that 2-formylfuran has received considerable attention both experimental and theoretical [2—13]. However, there are very few experimental and theoretical reports about the conformational preference, internal rotation barrier, and vibrational spectral analysis of 3-formylfuran [14, 15] but a detailed quantum chemical computation of the torsional potentials of formylfurans has not been performed. Such a study will contribute to a better understanding of many controversial aspects of their molecular structures, structural stability, and vibrational spectra. In this study, the molecular geometry, potential energy surface, and IR vibrational spectra of both 2-formylfuran and 3-formylfuran are investigated using the Gaussian 03 program package [16]. The energies of the possible conformers and the transition states of the molecules were optimized by Becke's three-parameter exchange functional [17] combined with the Lee—Yang—Parr [18] correlation functional (B3LYP) method using the standard 6-31+G* basis set. From the data, the relative conformational stability and the internal rotation barrier were determined. The effect of solvents on the conformational stability of the two molecules was investigated using the integral equation formalism in the polarizable continuum model (IEF-PCM) [19—21]. Furthermore, vibrational wavenumbers were also computed and a complete assignment of the fundamental vibrational modes was made based on the comparison of the computed and experimental results.

COMPUTATIONAL METHODS

The GAUSSIAN 03 program package was used to optimize the structures, predict energies and vibrational wavenumbers for 2-formylfuran and 3-formylfuran in their possible conformations (Scheme 1). The *trans* and *cis* conformers of the studied molecules are defined by the position of the carbonyl oxygen atom with respect to the furan ring oxygen atom (Scheme 1).
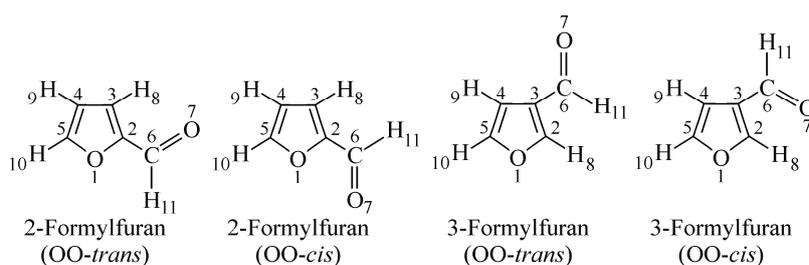
Scheme 1. Atom numbering for 2-formylfuran and 3-formylfuran in the *trans* and *cis* conformations

Computations were performed at the DFT-B3LYP level of theory, which had been previously used successfully in a variety of conformational studies [22—25]. The standard 6-31+G* basis set was used for all the atoms to carry out the computation utilizing the C_s symmetry of the molecules. Solvent effects on the conformational preference have been investigated using solvents with different polarities. Dielectric constants of 1.92, 4.90, 7.58, 10.36, 20.70, 24.55, 32.63, 46.70, and 78.39 were used as the values for heptane, chloroform, tetrahydrofuran, dichloroethane, acetone, ethanol, methanol, dimethylsulfoxide, and water, respectively. IEF-PCM was used for all solution phase computations. The infrared data are reported and each of the vibrational modes was visually confirmed by the Gauss-View program [26]. The wavenumbers ν_j, and intensities obtained from the computations were used to simulate the infrared spectra of *trans* and *cis* conformers of the two molecules.
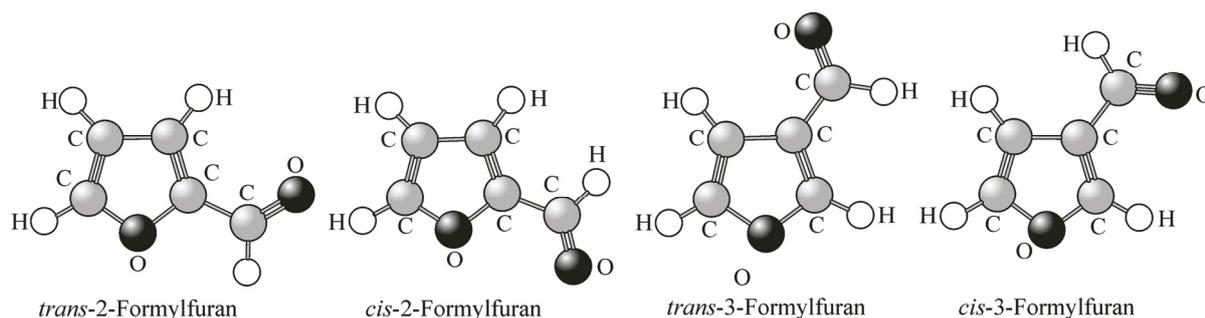
Fig. 1. Optimized structures of the *cis* and *trans* conformers of 2- and 3-formylfuran

RESULTS AND DISCUSSION

The rotation of the aldehyde group (CHO) on the furan rings of both 2-formylfuran and 3-formyl-furan leads to two equilibrium configurations (OO-*trans* and OO-*cis*). The preference between the two possible planar conformations of heterocycles such as formylfurans is often medium dependent because of the differences in polarity. Such intrinsic conformational preferences can be determined using theoretical methods. Thus, DFT calculations were performed at B3LYP/6-31+G* theoretical levels to find the most stable configurations. The optimized geometries of both *cis* and *trans* conformers of the studied molecules are shown in Fig. 1 and the geometry parameters are presented in Table 1. It is important to note that the computed bond lengths, bond angles, dipole moments, and rotational constants are in close agreement with the experimental microwave spectrum analysis of 2-formylfuran reported recently [10]. To be more specific, the root mean square errors for the *cis* conformer are 0.018 Å (bond length) and 1.8° (bond angle), while that of the *trans* conformers are 0.024 Å (bond length) and 2.0° (bond angle). The computation shows that the dipole moments of the *cis* conformers of both molecules are larger than those of the *trans* conformers. Computed total energies of the *trans*, *cis*, and transition states for the two molecules are presented in Table 2. Relative energies, corrected relative energies, and rotational barriers are also presented therein. From the computations, both 2-formylfuran and 3-formylfuran were predicted to exist in the planar *trans* position, where the two oxygen atoms are *trans* to one another (OO-*trans*). Generation of potential energy functions from the experimental data is a difficult task, since only conformations near the minima are appreciably populated. The alternative is to carry out accurate theoretical calculations for the appropriate numbers of rotational angles. Therefore, to study different conformations of these molecules, potential energy scans (PES) for the internal rotation of the aldehyde group (CHO) about the C—C single bond was performed at the B3LYP/6-31+G* level of theory. Torsion angles ϕ (O_1C_2—C_6O_7) in 2-formylfuran and ϕ (C_2C_3—C_6O_7) in 3-formylfuran were varied in steps of 15° from $\phi = 0°$ (*cis* position, where the two oxygen atoms are *cis* to one another) to $\phi = 180°$ (*trans* position, where the two oxygen atoms are *trans* to one another). The saddle points were determined and full geometry optimization was carried out at the transition state.

Fig. 2 shows the potential energy surface of the two molecules as a function of the dihedral angle (ϕ). The rotational energy profiles were obtained by optimizing the total energy at a fixed dihedral angle, and the other parameters were relaxed to their equilibrium values. All the reported minima along the potential energy surface were subjected to full geometry optimizations and the minimum was verified by computing the vibrational wavenumbers that resulted in the absence of imaginary wavenumbers. The highest energy conformer for the two molecules occurs at a dihedral angle close to 90° (where —CHO is almost perpendicular). This is referred to as the transi-
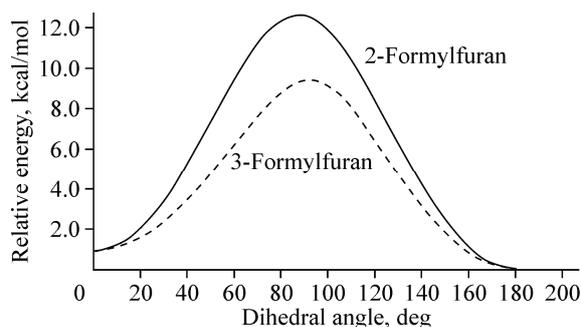
Fig. 2. Calculated potential surface for 2-formylfuran and 3-formylfuran

Optimized parameters, *dipole moments* (Debye), *and rotational constants* (MHz) *for*
2-formylfuran and 3-formylfuran computed by B3LYP *using the 6-31+G* basis set*

Geometry parameter	2-Formylfuran				3-Formylfuran	
	cis		trans		cis	trans
	Exp. [10]	Calc.	Exp. [10]	Calc.	Calc.	Calc.
Bond lengths (Å)						
O_1—C_2	1.34	1.37	1.35	1.38	1.35	1.35
C_2—C_3	1.35	1.37	1.33	1.38	1.37	1.37
C_3—C_4	1.43	1.42	1.44	1.42	1.44	1.44
C_4—C_5	1.36	1.37	1.36	1.37	1.36	1.36
C_5—O_1	1.36	1.35	1.36	1.35	1.37	1.38
C_n—C_6	1.49	1.46 (C_2)	1.50	1.46 (C_2)	1.47 (C_3)	1.46 (C_3)
C_6=O_7	1.21	1.22	1.22	1.22	1.22	1.22
C_n—H_8	—	1.08 (C_3)	—	1.08 (C_3)	1.08 (C_2)	1.08 (C_2)
C_4—H_9	—	1.08	—	1.08	1.08	1.08
C_5—H_{10}	1.07	1.08	1.08	1.08	1.08	1.08
C_6—H_{11}	1.11	1.11	1.11	1.11	1.11	1.11
Bond angles (deg.)						
$O_1C_2C_3$	113.4	109.6	113.7	109.5	110.3	110.5
$C_2C_3C_4$	105.2	106.6	104.7	106.5	105.8	105.9
$C_3C_4C_5$	105.6	105.7	106.7	106.1	106.2	106.0
$C_4C_5O_1$	111.3	111.1	110.9	110.8	110.1	110.5
$C_5O_1C_2$	104.8	107.0	104.7	107.0	107.5	107.0
$C_nC_6O_7$	125.0	125.6 (C_2)	123.1	123.7 (C_2)	124.6 (C_3)	124.3 (C_3)
$C_nC_6H_{11}$	113.7	113.0 (C_2)	115.6	114.7 (C_2)	115.0 (C_3)	115.2 (C_3)
Dipole moment (μ_t)						
	—	4.57	—	3.89	3.34	2.98
Rotational constants (MHz)						
A	8144	8139	8192	8190	8152	8286
B	2097	2084	2046	2031	1974	1964
C	1669	1659	1637	1628	1590	1586

Computed total energies and/or zero-point corrections (Hartrees), *and relative energy and rotational*
barriers (kcal/mol) *in 2-formylfuran and 3-formylfuran calculated at the* DFT-B3LYP/6-31+G* *level*

Level/parameter	2-formylfuran	3-formylfuran	Level/parameter	2-formylfuran	3-formylfuran
Total Energy			Zero-Point correction		
cis	−343.3691	−343.3666	cis	0.0795	0.0794
trans	−343.3704	−343.3681	trans	0.0794	0.0795
Transition state*	−343.3503	−343.3530	Transition state	0.0786	0.0788
Relative Energy	0.85	0.92	Corrected Relative energy	0.801	0.988
cis—trans barrier	11.78	8.51	Corrected cis—trans barrier	11.19	8.10
trans—cis barrier	12.63	9.43	Corrected trans—cis barrier	12.09	8.95

* Dihedral angle at the transition state was found to be 87.5 and 92.6 for 2-formylfuran and 3-formylfuran, resp.

tion states with one imaginary frequency. The trend of the torsional barriers is 2-formylfuran > 3-for-mylfuran, which is in agreement with the trends observed in torsional barriers of 2-, 3- and 4-formyl-pyridine [26].

The *cis—trans* internal rotation barrier for 2-formylfuran and 3-formylfuran are computed to be 11.19 kcal/mol^{-1} and 8.10 kcal/mol respectively. The computed internal rotation barrier for 3-formyl-furan is in agreement with the experimental value of 8.3 kcal/mol^{-1} as determined by the dynamic ^{13}C NMR analysis [15]. Similarly, the computed internal rotation for 2-formylfuran is in agreement with the experimental result obtained from IR spectroscopy [4]. The internal rotation barrier in 3-formyl-furan is lower than that found in 2-formylfuran, implying a lower conjugative interaction of the formyl group with the furan ring substituted at position 3 than in position 2 [14, 15], as illustrated in Scheme 2.
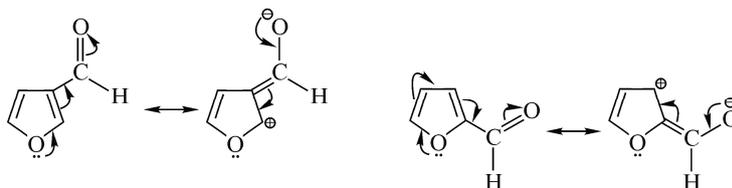
Scheme 2. Conjugation in 2-formylfuran and 3-formylfuran

It is important to note that the internal rotation barriers of the studied molecules are solvent de-pendent. Thus, the internal rotation barrier for 2-formylfuran determined in different solvents was re-ported to vary between 9.56 kcal/mol^{-1} and 11.71 kcal/mol^{-1} [7]. The total energies of the *trans* and *cis* conformers including the zero point corrections for both 2-formylfuran and 3-formylfuran are given in Table 2. For both molecules, the OO-*trans* conformers were found to be more stable than the *cis* con-formers. The relative energies were found to 0.8 kcal/mol^{-1} and 0.92 kcal/mol^{-1} for 2-formylfuran and 3-formylfuran respectively. The calculated relative energy is in good agreement with the experimental value of ≤ 1.0 kcal/mol obtained from the IR and Raman spectroscopy study of 2-formylfuran in the vapor phase [3]. There are no gas-phase experimental data for 3-formylfuran for comparison with the computed relative energy. It is well known that the equilibrium position between alternative rotational isomers of a particular molecule can be remarkably medium dependent. In order to establish the preferred conformations in solution, the IEF-PCM model implemented at the B3LYP/6-31+G* level of theory was applied to the two molecules investigated. Fig. 3 shows variation of the *cis—trans* relative energy with the dielectric constant of the solvent obtained from the IEF-PCM optimization at the B3LYP/6-31+G* level of theory. The *trans* conformer of 2-formylfuran, which is more stable in the gas phase, becomes less stable as the dielectric constant of the solvent increases. This is expected because the conformer with a high dipole moment is generally more favored in the medium of dielectric constant, and this result is consistent with the experimental data reported. However, the effect of solvents is not large enough to reverse the order of stability between the *cis* and *trans* conformers of 3-formylfuran. *trans*-3-Formylfuran is more stable in solution relative to the gas phase and the stability increases with an increase in the dielectric constant of the solvent. In general, the *cis* conformer of 2-formylfuran be-comes more stable in solution relative to the gas phase, while the *trans* conformer of 3-formylfuran remains as the most stable conformer in both gas and solution phases.

The optimized structural parameters were used to compute the vibrational wavenumbers for the two molecules. Tables 3 and 4 present the computed vibra-tional wavenumbers and proposed vibrational assignments for the *cis* and *trans* conformers of the two studied furan derivatives. These computations for the two molecules re-sult in twenty seven IR and Raman active fundamental vi-brations that belong to only two irreducible representations of the C_s point group, 19 belonging to *A'* (in-plane) modes, and 8 to *A''* (out-of-plane) modes. Unfortunately, there are
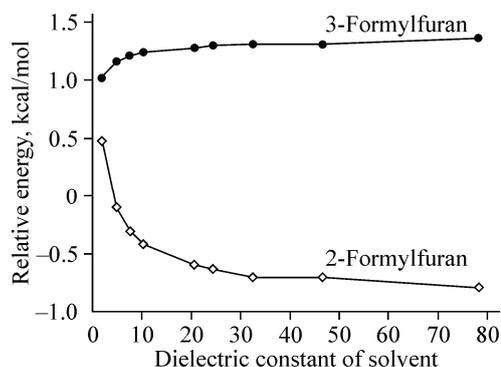
Fig. 3. Variation of the relative energy with the dielectric constant of the solvent

Calculated vibrational wavenumbers (cm^{-1}) *of trans and cis* 2-*formylfuran computed at the* B3LYP/6-31+G* *level*

No.	Sym.	trans			cis			Assignment
		Exp. [5]	Calc Freq	ν_{expt}/ν_{calc}	Exp. [5]	Calc Freq	ν_{expt}/ν_{calc}	
ν_1	A'	3150	3295	0.96	3150	3294	0.96	C—H stretching
ν_2	A'	3144	3281	0.96	3144	3272	0.96	C—H stretching
ν_3	A'	3128	3266	0.96	3128	3261	0.96	C—H stretching
ν_4	A'	2804	2954	0.95	2841	2930	0.97	C—H stretching (CHO)
ν_5	A'	1694	1758	0.96	1694	1765	0.96	C=O stretching
ν_6	A'	1577	1614	0.98	1577	1606	0.98	C—C + C=O stretching
ν_7	A'	1473	1500	0.98	1479	1509	0.98	C=C stretching
ν_8	A'	1399	1446	0.97	1399	1436	0.97	C=C stretching
ν_9	A'	1365	1402	0.97	1394	1398	1.00	CHO deformation
ν_{10}	A'	1277	1272	1.00	1277	1299	0.98	C—O stretching
ν_{11}	A'	1242	1226	1.01	1271	1250	1.02	CH bending + C—C str
ν_{12}	A'	1152	1182	0.97	1164	1197	0.97	CH bending + C=C str
ν_{13}	A'	1085	1118	0.97	1085	1115	0.97	CH bending + C—O str
ν_{14}	A'	1011	1040	0.97	1018	1046	0.97	C—O stretching
ν_{15}	A''	947	1010	0.94	933	1003	0.93	C—O stretching
ν_{16}	A'	888	963	0.92	888	948	0.94	Ring bending
ν_{17}	A''	882	909	0.97	882	900	0.98	CH bending
ν_{18}	A'	830	897	0.93	830	898	0.92	CH bending
ν_{19}	A''	825	851	0.97	825	845	0.98	CH bending
ν_{20}	A''	756	774	0.98	759	777	0.98	CH bending
ν_{21}	A'	746	756	0.99	746	764	0.98	ring bending
ν_{22}	A''	639	639	1.00	621	651	0.95	ring rocking
ν_{23}	A''	595	604	0.99	595	603	0.99	ring rocking
ν_{24}	A'	495	496	1.00	498	501	0.99	CHO deformation
ν_{25}	A''	245	250	0.98	280	291	0.96	C—C bending
ν_{26}	A'	213	208	1.02	213	205	1.04	C—CHO bending
ν_{27}	A''	145	157	0.92	134	137	0.98	C—CHO bending

Calculated vibrational wavenumbers (cm^{-1}) *of trans and cis* 3-*formylfuran computed at the* B3LYP/6-31+G* *level*

No.	Sym.	trans	cis	Assignment	No.	Sym.	trans	cis	Assignment
ν_1	A'	3307	3307	C—H stretching	ν_{15}	A''	1014	1021	C—O stretching
ν_2	A'	3287	3303	C—H stretching	ν_{16}	A'	989	1000	Ring bending
ν_3	A'	3281	3263	C—H stretching	ν_{17}	A''	886	886	CH bending
ν_4	A'	2924	2928	C—H stretching (CHO)	ν_{18}	A'	885	868	CH bending
ν_5	A'	1766	1767	C=O stretching	ν_{19}	A''	816	833	CH bending
ν_6	A'	1609	1603	C—C + C=O stretching	ν_{20}	A''	753	756	CH bending
ν_7	A'	1546	1537	C=C stretching	ν_{21}	A'	751	743	ring bending
ν_8	A'	1440	1448	C=C stretching	ν_{22}	A''	622	620	ring rocking
ν_9	A'	1405	1389	CHO deformation	ν_{23}	A''	613	615	ring rocking
ν_{10}	A'	1306	1292	C—O stretching	ν_{24}	A'	493	487	CHO deformation
ν_{11}	A'	1257	1253	CH bending + C—C str	ν_{25}	A''	282	253	C—C bending
ν_{12}	A'	1193	1192	CH bending + C=C str	ν_{26}	A'	198	200	C—CHO bending
ν_{13}	A'	1108	1110	CH bending + C—O str	ν_{27}	A''	140	135	C—CHO bending
ν_{14}	A'	1032	1043	C—O stretching					
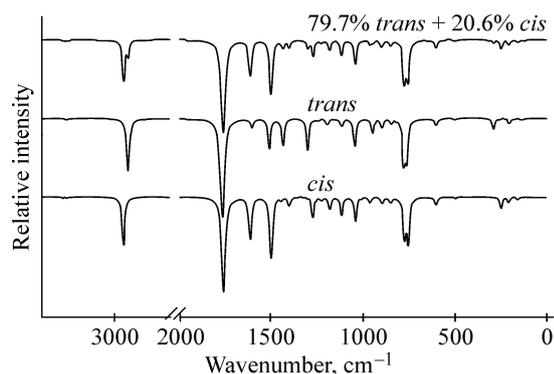
Fig. 4. Computed vibrational infrared spectrum of 2-formylfuran for the *cis* and *trans* mixture, pure *trans*, and pure *cis* at the DFT-B3LYP/6-31+G* level
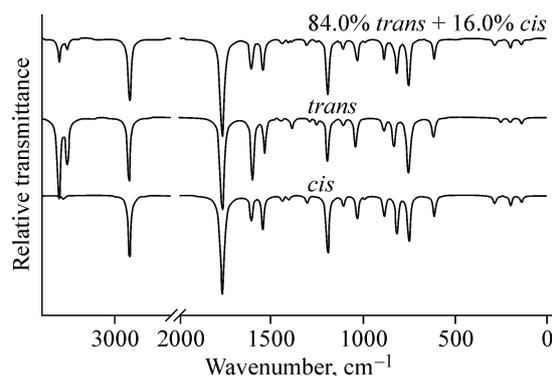
Fig. 5. Computed vibrational infrared spectrum of 3-formylfuran for the *cis* and *trans* mixture, pure *trans*, and pure *cis* at the DFT-B3LYP/6-31+G* level

no vapor-phase infrared spectral data with which the computed vibrational wavenumbers for 3-formylfuran can be compared. However, the comparison of the calculated vibrational wavenumbers for 2-formylfuran with the experimental values reflects reasonable agreement for them. The ratios of the experimental and computed vibrational wavenumbers were calculated to be between 0.92—1.02, and 0.92—1.04 for *trans*-2-formylfuran, and *cis*-3-formylfuran respectively. These ratios reflect a high level of conformity between the harmonic wavenumbers obtained from the DFT computation and the observed fundamental wavenumbers. The normal modes associated with individual vibrations were graphically displayed using the GaussView program. By combining the motions observed using the GaussView program and infrared band intensities with the experimental results reported, complete vibrational frequency assignments were made with a high degree of confidence. The vibrational infrared spectra were computed as described previously [23] and the simulated IR spectra of the two molecules clearly show the difference in the spectral characteristics of the two conformers (Figs. 4 and 5). The percentages of the *trans* conformers in the vapor phase at a temperature of 298.15 K were estimated to be 79.7 % and 84.0 % for 2-formylfuran and 3-formylfuran respectively. The relative populations of the conformers depend on the differences in their free energies. As such, 2-formylfuran, which has a free energy difference (ΔG) of 0.94 kcal/mol, has a higher percentage of the *trans* conformer than 3-formylfuran that has a free energy difference (ΔG) of 0.82 kcal/mol.

CONCLUSIONS

Density functional theory geometry optimizations have been performed for the possible conformers and the transition state of the two derivatives of formylfuran using the Gaussian 03 package. The potential energy curves were obtained for the rotational angles ϕ (O_1C_2—C_6O_7) of 2-formylfuran and ϕ (C_2C_3—C_6O_7) of 3-formylfuran. From the computations both molecules were predicted to exist predominantly in the *trans* conformation with the *cis-trans* rotational barriers of 11.19 kcal/mol^{-1} for 3-formylfuran and 8.10 kcal/mol^{-1} for 2-formylfuran, The normal modes and the corresponding vibrational assignment of the two molecules were theoretically examined. A complete assignment of the fundamental vibrational modes is proposed based on the Gaussian view visualization program and experimental results. Infrared intensities were helpful in making the assignments of the fundamental vibrational modes. Theoretical gas phase infrared spectra of the pure conformers and their mixtures at a temperature of 298.15 K are reported. The *trans* conformers of the two molecules predominate with around 79.9 % and 84.0 % of the equilibrium mixtures in the gas phase for 2-formylfuran and 3-formylfuran respectively. The relative populations of the conformers reflect the differences in the free energies of the studied molecules. The computations of solvent effects were performed over nine different values of the dielectric constant to illustrate the effects of the varying dielectric constant using the IEF-PCM method. It is found that the *cis* conformer of 2-formylfuran becomes more stable

in solution relative to the gas phase, while the *trans* conformer of 3-formylfuran remains as the most stable conformer in both gas and solution phases.

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