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DENSITY FUNCTIONAL THEORY STUDIES OF CONFORMATIONAL STABILITIES AND ROTATIONAL BARRIERS OF 2- AND 3-THIOPHENECARBOXALDEHYDES

Y. Umar[1], J. Tijani[2], S. Abdalla[3]

[1]*Department of Chemical and Process Engineering Technology, Jubail Industrial College, Jubail Industrial City, Saudi Arabia*
E-mail: umar_y@jic.edu.sa
[2]*Department of General Studies, Jubail Industrial College, Jubail Industrial City, Saudi Arabia*
[3]*Department of Chemistry, Faculty of Science, University of Khartoum, P.O. Box 321, Khartoum, Sudan*

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The molecular structures, conformational stabilities, and infrared vibrational wavenumbers of 2-thiophenecarboxaldehyde and 3-thiophenecarboxaldehyde are computed using Becke-3—Lee—Yang—Parr (B3LYP) with the 6-311++G** basis set. From the computations, *cis*-2-thiophenecarboxaldehyde is found to be more stable than the transfer conformer with an energy difference of 1.22 kcal/mol, while *trans*-3-thiophenecarboxaldehyde is found to be more stable than the *cis* conformer by 0.89 kcal/mol. The computed dipole moments, structural parameters, relative stabilities of the conformers and infrared vibrational wavenumbers of the two molecules coherently support the experimental data in the literature. The normal vibrational wavenumbers are characterized in terms of the potential energy distribution using the VEDA4 program. The effect of solvents on the conformational stability of the molecules in nine different solvents is investigated using the polarizable continuum model.

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Keywords: density functional method, rotational barrier, vibrational wavenumber, solvent effect, thiophenecarboxaldehyde, conformational preference, infrared spectra, geometry optimization, polarizable continuum model, potential energy distribution (PED).

INTRODUCTION

The conformational preference of heterocyclic compounds has recently been the subject of several experimental and theoretical studies [1—7]. The molecules of 2-thiophenecarboxaldehyde (hereinafter called 2-TC) and 3-thiophenecarboxaldehyde (hereinafter called 3-TC) are thiophene derivatives that contain an aldehyde (—CHO) group substituted at positions 2 and 3 to the sulfur atom of the thiophene ring. The rotation of the aldehyde group (CHO) on the thiophene rings of these compounds leads to two equilibrium configurations (isomers). Thus, both 2-TC and 3-TC can exist in two asymmetric planar rotational conformers whereby the sulfur and oxygen atoms can be either OS-*cis* or OS-*trans*. Several experimental and theoretical studies have confirmed the coexistence and the stability of the *cis* and *trans* conformers of these molecules [4, 5, 8—10]. The presence and stability of the *cis* and *trans* conformers of 2-TC have been examined through microwave [8], infrared [9], ^{1}H NMR [10] and electron diffraction spectroscopy, and it was concluded that the *cis* conformer is most stable. Lodovic et al. [10] investigated the inter conversion barriers in 2-TC and 3-TC by low-temperature ^{13}C NMR and reported the rotational free activation energies in favor of OS-*cis* of 2-TC and OS-*trans* of 3-TC as the more stable conformers. Recently, the coexistence of the two conformers (*cis* and *trans*) of 2-TC and 3-TC has been reported by IR matrix isolation spectroscopy combined with UV photo excitation and DFT calculations [5].

These thiophene carboxaldehydes have applications in agriculture [11], pharmaceuticals and pesticides [12, 13], cosmetics [14], herbicides [15], and the synthesis of Schiff bases [16—21]. These Schiff bases are the well-known class of ligands used in the synthesis of metal complexes that have potential applications in materials chemistry and biochemistry [16—21]. In addition, 2-TC is used as a cross-linker in the synthesis of chitosan hydrogel film that provides photosensitivity to chitosan biomolecules for optical, biomedical, and bio-sensing applications [22].

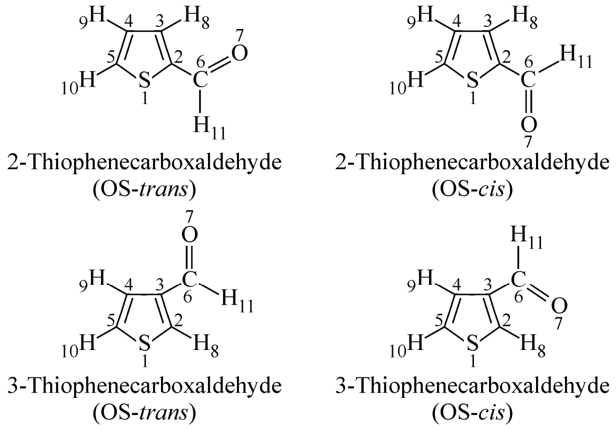
In general, the conformational preferences and stability of two possible rotational conformers of monosubstituted heterocylic compounds such as thiophene, furan, and pyrrole are strong solvent dependent due to differences in their polarity [23]. Thus, the ability to reliably predict the conformational preference and the rotational barrier is of great interest for systems where the experimental conformational preference is not clear and is strongly solvent dependent. There are very few theoretical reports about the conformational preference, internal rotation barrier, and vibrational spectral analysis of 3-TC. Likewise, a detailed quantum chemical computation of the torsional potentials of TCs 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 addition, the molecular conformation and vibrational data of these molecules are very significant for many applications and in the understanding of the structures and properties of these molecules. Therefore, owing to the increasing interest in and the importance of TCs as derivatizing agents, corrosion inhibitors and in the synthesis of Schiff base ligands, we thought it worthy to take up theoretical studies to support and complement the experimental reports since computational studies are reliable and useful with respect to the structural and vibrational properties of molecules. Thus, the aim of this work is to take advantage of the quantum mechanical calculations to carry out a systematic study on the molecular geometry and vibrational spectra which will give a deep insight into the properties of the title molecules and aid in clarifying and complementing the available experimental data. Furthermore, it is of interest to compare the results for TCs with those for the related compounds such as furancarboxaldehye and others. In this study, the molecular geometry, potential energy surface, and IR vibrational spectra of both 2-TC and 3-TC were theoretically investigated by means of density functional theory (DFT) calculations. The results for TCs were compared with the available experimental data [8, 9] and analogous compounds such as furancarboxaldehyde (C_4H_3O—CHO) and selenophenecarboxaldehyde (C_4H_3Se—CHO) [3, 7]. This paper provides the additional quantitative chemical knowledge and the detailed insight into the structural stability, molecular structure, rotational barrier, vibrational spectra and the assignment of vibrational modes of these compounds [3, 7].

COMPUTATIONAL METHODS

The GAUSSIAN 09 program package [24] was used to optimize the structures, predict the energies and vibrational wavenumbers for 2-TC and 3-TC 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 thiophene ring sulfur (Scheme 1).

Computations were performed at the DFT-B3LYP level of theory, which has been previously used successfully in a variety of conformational studies [2—6]. The energies of the possible conformers and the transition states of the molecules were optimized by Becke's three-parameter exchange functional [25] combined with the Lee—Yang—Parr [26] correlation functional (B3LYP) method using the standard 6-311++G** basis set. From the data, the relative conformational stability and the barrier to internal rotation were determined. The effect of solvents on the conformational preference was 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. The integral equation formulation (IEF) [27—31] version of PCM [32—34] was used as a solvation model for all solution phase computations. Furthermore, vibrational wavenumbers were also



Scheme 1. Atom numbering for 2-TC and 3-TC in the *trans* and *cis* conformations

computed and the assignment of the fundamental vibrational modes was performed based on PED using the VEDA 4 program [35] combined with the animation option of the GaussView graphical interface of the Gaussian program [36]. 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.

RESULTS AND DISCUSSION

The rotation of the aldehyde group (CHO) on the furan rings of both 2-TC and 3-TC leads to two equilibrium configurations (OS-*trans* and OS-*cis*). The preference between the two possible planar conformations of the heterocycle such as TC is often medium dependent because of differences in the polarity. Such intrinsic conformational preferences can be determined using theoretical methods. Thus, DFT calculations were performed at the B3LYP/6-311++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

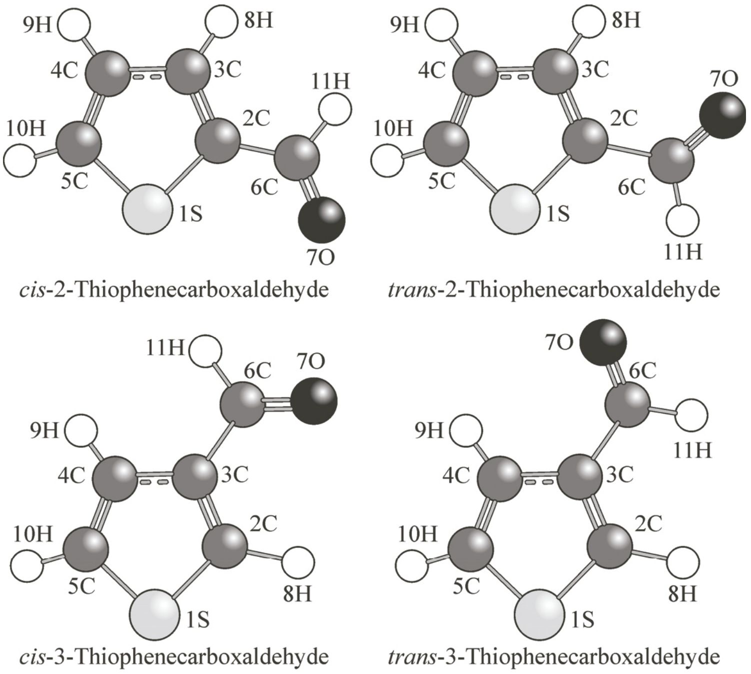


Fig. 1. Optimized structures of the *cis* and *trans* conformers of 2-TC and 3-TC

Table 1

Optimized parameters, dipole moments (Debye), *and rotational constants* (MHz) *for* 2-TC *and* 3-TC *computed at the* B3LYP *level using the* 6-311++G** *basis set in the gas phase*

Geometrical parameter[a]	2-TC			3-TC	
	Expt[b]	Calculated		Calculated	
		cis	*trans*	*cis*	*trans*
Bond lengths, Å					
S_1—C_2	1.72	1.75	1.75	1.72	1.72
C_2—C_3	1.38	1.38	1.38	1.38	1.38
C_3—C_4	1.43	1.42	1.42	1.43	1.43
C_4—C_5	1.43	1.37	1.37	1.36	1.36
C_5—S_1	1.72	1.72	1.72	1.74	1.74
C—C_6	1.47	1.46(C_2)	1.46(C_2)	1.47(C_3)	1.47(C_3)
$C_6{=}O_7$	1.22	1.21	1.21	1.21	1.21
C—H_8	1.11	1.08(C_3)	1.08(C_3)	1.08(C_2)	1.08(C_2)
C_4—H_9	1.11	1.08	1.08	1.08	1.08
C_5—H_{10}	1.11	1.08	1.08	1.08	1.08
C_6—H_{11}	1.11	1.11	1.11	1.11	1.11
Bond angles, deg.					
$S_1C_2C_3$	111.8	111.2	110.9	111.7	111.8
$C_2C_3C_4$	112.2	113.0	113.0	112.3	112.4
$C_3C_4C_5$	112.2	112.1	112.6	112.8	112.5
$C_4C_5S_1$	111.8	112.7	112.2	111.3	111.8
$C_5S_1C_2$	92.0	90.9	91.3	91.9	91.5
CC_6O_7	123.7	125.3(C_2)	124.0(C_2)	125.0(C_3)	124.5(C_3)
CC_6H_{11}	—	113.6(C_2)	115.4(C_2)	114.6(C_3)	114.8(C_3)
Dipole moment (μ_t)					
	3.52[c]	4.13	3.66	3.41	3.22
Rotational constants, MHz					
A	5113	5058	5607	6014	6792
B	1888	1871	1776	1535	1464
C	1379	1366	1311	1223	1205

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[a] The atom numbering is given in Scheme 1.

[b] Taken from [9].

[c] Taken from [8].

the computed bond lengths, bond angles, dipole moments and rotational constants are in close agreement with the experimental microwave spectrum of 2-TC reported recently [8]. To be more specific, the root mean square errors for the *cis* conformer are 0.027 Å (bond length) and 0.97° (bond angle), while those of the *trans* conformers are 0.027 Å (bond length) and 0.63° (bond angle). It is well known that those conformational interconversion lead to a variation of molecular parameters such as dipole moments, rotational constants, molecular polarazability, vibrational wavenumbers, intensities and amplitudes of molecular vibrations. The computation shows that there are no significant variations in the computed geometry parameters (bond lengths and bond angles) of the two conformers. However, the

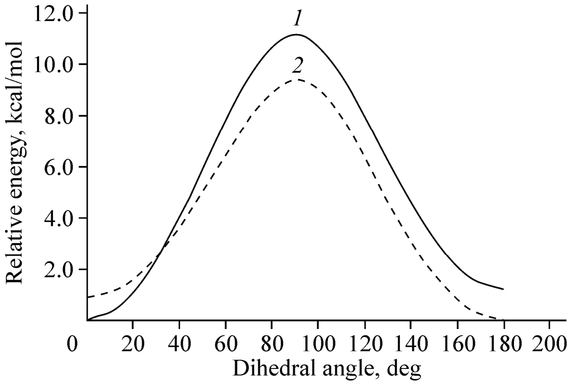

Fig. 2. Calculated potential energy profile for 2-TC (*1*) and 3-TC (*2*)

dipole moments of the *cis* conformers of both molecules are slightly higher than those of the corresponding *trans* conformers. In addition, the computed dipole moments for the studied molecules are similar in magnitude to the dipole moments of their analogues furancarboxaldehyde (O,O-system) and selenophenecarboxaldehyde (Se,O-system). For example, the dipole moments of 2-furancarboxaldehyde, 2-TC, and 2-selenophenecarboxaldehyde computed at B3LYP/6-311++G** are 4.52 D [7], 4.13 D (Table 1), and 3.94 D [3] respectively. The same trend was observed for the computed dipole moments of 3-TC and its O, O and Se, O analogues. These variations in dipole moments reflect the differences in the electronegativity of heteroatoms (O, S, and Se) in the five-membered rings.

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, the potential energy scan (PES) for the internal rotation of the aldehyde group (CHO) about the C—C single bond was performed at the B3LYP/6-311++G** level of theory. Torsional angles $\phi(\mathrm{S_1C_2{—}C_6O_7})$ in 2-TC and $\phi(\mathrm{C_2C_3{—}C_6O_7})$ in 3-TC were varied in steps of 15° from $\phi = 0°$ (*cis* position, where the ring sulfur and oxygen atoms are *cis* to one another) to $\phi = 180°$ (*trans* position, the ring sulfur and oxygen atoms are *trans* to one another). The saddle points were determined, and the full geometry optimization was carried out in the transition state. Fig. 2 shows the potential energy profile 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, which 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 virtually perpendicular). This is referred to as the transition states with one imaginary vibrational wavenumber characterizing the saddle point. The transition states of 2-TC and 3-TC are located at the dihedral angles of 90.5° and 91.6° respectively. The calculated rotational barrier in 3-TC (8.55 kcal/mol) is smaller than that of 2-TC (9.15 kcal/mol), which is in agreement with analogous furancarboxaldehyde. The lower rotational energy profiles of these heterocycles have been attributed to the lower conjugative interaction of the aldehyde (—CHO) group with the heterocyclic ring substituted at position 3 rather than in position 2 [37].

The calculated relative energies in the gas phase $((\Delta E = E_{trans} - E_{cis}))$ show that *cis* 2-TC is more stable than the *trans* conformer by 1.18 kcal/mol and *trans* 3-TC is more stable than the *cis* conformer by 0.81 kcal/mol, which is an excellent agreement with the IR experimental data [5] where the *cis* conformer of 2-TC is favored by 1.07 kcal/mol and the trans conformer is favored by 0.89 kcal/mol. The conformational preference of 2-TC is similar to analogous 2-selenophenecarboxaldehyde, where the *cis* conformer is reported to be more stable by 1.84 kcal/mol. The situation is quite different from that of analogous furancarboxaldehyde, for which the *cis* conformers of both 2- and 3-furancarboxaldehydes are reported to be more stable than the *trans* conformers by 0.85 and 0.92 kcal/mol respectively. It is well known that the equilibrium position between the alternative rotational isomers of a particular molecule can be remarkably medium dependent. In order to establish the preferred conformations in solution, PCM implemented at the B3LYP/6-311++G** level of theory was used to investigate the conformational preference of 2-TC and 3-TC in nine different solvents. The computed relative energies (kcal/mol) of 2-TC and 3-TC in the gas and solution phases are provided in Table 2. It is

Table 2

Computed relative energies (kcal/mol), *of* 2-*thiophenecarboxaldehyde* (2-TC) *and* 3-*thiophenecarboxaldehyde* (3-TC) *in the gas phase and different solvents*

Solvent	Dielectric constant	2-TC		3-TC	
		ΔE	% *Cis* at 298.15 K	ΔE	% *Cis* at 298.15 K
Gas phase	—	1.22	87.34	–0.89	21.18
Heptane	1.92	1.32	89.03	–0.93	20.11
Chloroform	4.90	1.46	90.99	–0.98	18.23
Tetrahydrofuran	7.58	1.52	91.64	–1.00	17.62
Dichloroethane	10.36	2.22	97.25	–0.93	19.45
Acetone	20.70	1.59	92.43	–1.03	16.74
Ethanol	24.55	1.60	92.52	–1.03	16.67
Methanol	32.63	1.61	92.61	–1.04	16.56
Dimethylsulfoxide	46.70	1.62	92.71	–1.04	16.48
Water	78.39	1.63	92.79	–1.04	16.39

interesting to note that the gas phase relative energies for the two molecules are in good agreement with the literature values computed at different levels of theory [5]. The *cis* conformers of 2-TC, which is a more stable conformer in the gas phase, remained more stable in all the solvents, and the stability increased with an increase in the solvent dielectric constant. However, in the case of analogous 2-furancaboxaldehyde, the *trans* conformer, which is more stable in gas phase, becomes less stable as the dielectric constant of the solvent increases, but the effect of solvents is not large enough to reverse the stability [38]. In the case of 3-TC, the *trans* conformer, which is a more stable conformer, remained the more stable conformer in all the solvents; this is in contrast with analogous 3-furancarboxaldehyde where the *trans* conformer is more stable in solution relative to the gas phase [38]. The percentage of *cis* conformers at 298.15 K for 2-TC and 3-TC are given in Table 2. The percentage of the *cis* conformer has been calculated using k_{eq} derived from $\Delta G = RT\ In\ k_{\mathrm{eq}}$. The optimized structural parameters were used to compute the vibrational wavenumbers for the two molecules. Tables 3 and 4 present the computed vibrational wavenumbers and proposed vibrational assignments for the *cis* and *trans* conformers of the two studied molecules. These computations for the two molecules result in twenty seven IR fundamental vibrations 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. The simulated IR spectra of the two molecules clearly show the difference in the spectral characteristics of the two conformers (Figs. 3 and 4). A comparison of the results of the calculated vibrational wavenumbers for

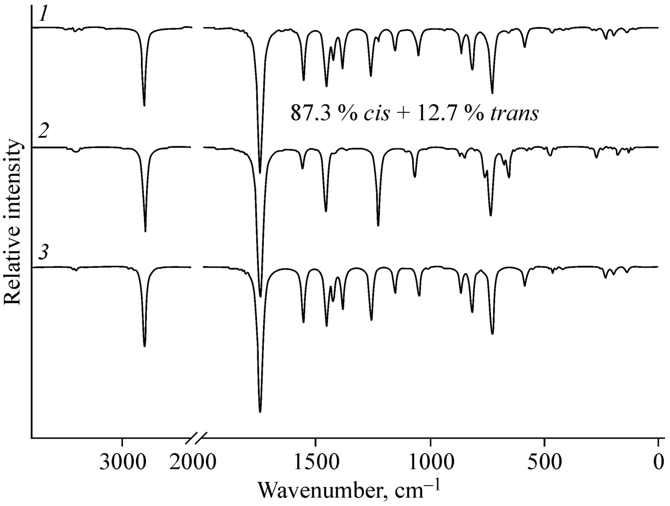

Fig. 3. Simulated vibrational infrared spectrum of 2-TC for the *cis* and *trans* mixture (*1*), pure *trans* (*2*) and pure *cis* (*3*) at the DFT-B3LYP/6-311++G** level

Table 3

Calculated vibrational wavenumbers (cm^{-1}) *of trans and cis* 2-TC *computed at the* B3LYP/6-311++G** *level*

No.	Sym.	*Trans*			*Cis*			Assignment (PED ≥ 5 %)
		Expt.[a]	Calc. freq.	ν_{expt} / ν_{calc}	Expt.[a]	Calc. freq.	ν_{expt} / ν_{calc}	
ν_1	A'	—	3242	—	3121	3238	0.96	υCH (90)
ν_2	A'	—	3221	—	3099	3211	0.97	υCH (84)
ν_3	A'	—	3204	—	3086	3196	0.97	υCH (90)
ν_4	A'	—	2904	—	2821	2900	0.97	υCH in CHO (99)
ν_5	A'	1705	1745	0.98	1705	1745	0.98	υCO (89)
ν_6	A'	1519	1556	0.98	1524	1560	0.98	υCC (58) + δHCC (18)
ν_7	A'	1432	1454	0.98	1425	1456	0.98	υCC (56) + δHCC (10) + δHCO (10)
ν_8	A'	1393	1425	0.98	1380	1417	0.97	δHCC (15) + δHCO (51)
ν_9	A'	1358	1383	0.98	1340	1364	0.98	υCC (17) + δHCS (23) + δHCO (26)
ν_{10}	A'	1241	1260	0.98	1232	1246	0.99	δHCC (49) + δHCS (10)
ν_{11}	A'	1146	1155	0.99	1211	1227	0.99	υCC (63) + δCCC (10)
ν_{12}	A'	1079	1102	0.98	1084	1106	0.98	υCC (18) + δHCC (26) + δHCS (47)
ν_{13}	A'	1034	1051	0.98	1044	1067	0.98	υCC (35) + δHCC (47)
ν_{14}	A''	—	1007	—	990	1009	0.98	τCCOH (94)
ν_{15}	A''	—	937	—	911	928	0.98	τHCCH (89)
ν_{16}	A'	862	867	0.99	864	872	0.99	υSC (29) + δCCC (52) + δCCO (11)
ν_{17}	A''	844	862	0.98	834	850	0.98	τHCCC (90)
ν_{18}	A'	815	817	1.00	760	760	1.00	υSC (37) + δCCO (11) + δCCC (43)
ν_{19}	A'	749	747	1.00	720	734	0.98	τHCCS (92)
ν_{20}	A''	718	729	0.98	672	677	0.99	υSC (21) + δCCO (64)
ν_{21}	A'	583	587	0.99	665	656	1.01	υCC (12) + δCCC (68)
ν_{22}	A''	—	572	—	566	575	0.98	τCCCC (84)
ν_{23}	A''	464	463	1.00	471	475	0.99	τCSCC (90)
ν_{24}	A'	420	419	1.00	454	455	1.00	υCC (36) + δCCC (40)
ν_{25}	A''	238	232	1.03	257	272	0.94	τCCSC (86)
ν_{26}	A'	195	195	1.00	173	176	0.98	δCCO (86)
ν_{27}	A''	—	138	—	122	130	0.94	τCCSC (85)

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[a] Taken from [4].

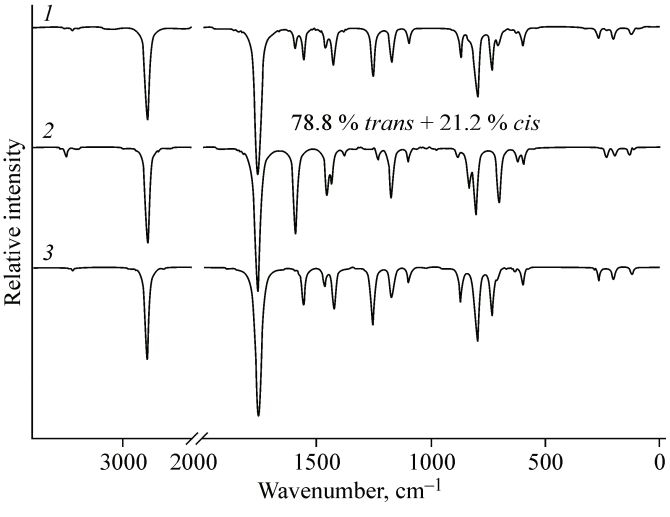

Fig. 4. Simulated vibrational infrared spectrum of 2-TC for the *cis* and *trans* mixture (*1*), pure *trans* (*2*) and pure *cis* (*3*) at the DFT-B3LYP/6-311++G** level

Table 4

Calculated vibrational wavenumbers (cm^{-1}) *of trans and cis* 3-TC *computed at the* B3LYP/6-311++G** *level*

No.	Sym.	*Trans*			*Cis*			Assignment (PED ≥ 5 %)
		Expt.[a]	Calc. freq.	ν_{expt} / ν_{calc}	Expt.[a]	Calc. freq.	ν_{expt} / ν_{calc}	
ν_1	A'	—	3245	—	—	3251	—	υCH (99)
ν_2	A'	—	3235	—	—	3246	—	υCH (99)
ν_3	A'	—	3220	—	—	3199	—	υCH (100)
ν_4	A'	—	2896	—	—	2894	—	υCH in CHO (99)
ν_5	A'	1706	1756	0.97	1710	1760	0.97	υCO (90)
ν_6	A'	1525	1558	0.98	1517	1594	0.95	υCC (63) + δCCO (10)
ν_7	A'	—	1465	—	—	1456	—	υCC (64) + δHCO (15)
ν_8	A'	1405	1426	0.99	1429	1436	1.00	υCC (33) + δCCO (13) + δHCC (18) + + δHCO (11)
ν_9	A'	—	1392	—	1340	1380	0.97	δHCO (61)
ν_{10}	A'	1236	1255	0.98	1213	1231	0.99	υCC (12) + δHCC (67)
ν_{11}	A'	1148	1172	0.98	1151	1174	0.98	υCC (15) + δHCS (63)
ν_{12}	A'	1074	1097	0.98	1076	1100	0.98	υCC (13) + δHCC (71)
ν_{13}	A'	938	1017	0.92	—	1019	—	δHCC (47) + τCCCO (18)
ν_{14}	A''	—	952	—	959	972	—	υCC (41) + δCCO (15) + δCCC (12)
ν_{15}	A''	—	920	—	828	900	—	τHCCS (81)
ν_{16}	A'	870	870	1.00	880	883	—	υSC (58) + δCCO (23)
ν_{17}	A''	783	813	0.96	838	834	—	υCC (16) + δCCC (61)
ν_{18}	A'	787	798	0.99	793	806	—	τHCSC (85)
ν_{19}	A'	727	734	0.99	—	702	—	δCCO (63)
ν_{20}	A''	—	710	—	—	701	—	τHCSC (89)
ν_{21}	A'	—	631	—	—	620	—	δCCO (72)
ν_{22}	A''	—	599	—	—	596	—	τHCSC (10) + τCCCC (71)
ν_{23}	A''	—	463	—	—	468	—	τCCCS (84)
ν_{24}	A'	—	436	—	—	459	—	υCC (26) + υSC (18) + δCCO (40)
ν_{25}	A''	—	268	—	—	232	—	τHCCC (13) + τCCCC (10) + τCCCO (72)
ν_{26}	A'	—	201	—	—	196	—	δCCC (86)
ν_{27}	A''	—	121	—	—	130	—	τCCCO (85)

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[a] Taken from [5].

2-TC with the experimental values reflects reasonable agreement for the vibrational wavenumbers. The ratios of the experimental and unscaled vibrational wavenumbers were calculated to be between 0.92—1.03, and the correlations are 0.9999 for *cis*-2-TC, 0.9998 for *trans*-2-TC, 0.9942 for *cis*-3-TC, 0.9962 for *trans*-3-TC. These ratios and correlations reflect a high level of conformity between the harmonic wavenumbers obtained from the DFT computation and the observed fundamental wavenumbers.

CONCLUSIONS

DFT geometry optimizations were performed for the possible conformers and transition state of 2-TC and 3-TC using Gaussian 09. The potential energy curves were obtained for the rotational angles $\phi(S_1C_2—C_6O_7)$ in 2-TC and $\phi(C_2C_3—C_6O_7)$ in 3-TC. From the computations it follows that *cis* 2-TC is more stable than the *trans* conformer by 1.18 kcal/mol and *trans* 3-TC is more stable than the *cis* conformer by 0.81 kcal/mol. Likewise, the rotational barriers are found to be 8.55 and 9.15 kcal/mol for 3-TC and 2-TC respectively. 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 PED using the VEDA 4 program and the animation option of the Gauss View graphical interface of the Gaussian program. The computations of solvent effects were performed over nine different values of the dielectric constant to illustrate the effects of dielectric constant variation using PCM methods. The results are in good agreement with the available experimental data.

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