DFT/TDDFT INVESTIGATION ON THE ELECTRONIC STRUCTURES AND SPECTRAL CHARACTERISTICS OF C_5H_3XOS (X = H, F, Cl OR Br)

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Halogen and solvent effects on the conformational, vibrational, and electronic characteristics of thiophene-2-carbaldehyde (T2C, C_5H_4OS) and thiophene-2-carbonyl-halogens [C_5H_3XOS, X = F (T2C-F), Cl (T2C-Cl), and Br (T2C-Br)] are analyzed by the density functional theory (DFT) and time dependent density functional theory (TDDFT), using the B3LYP functional and the 6-31++G(d,p) basis set. Computations consider two conformations of the compounds in both gas phase and solution. The present study aims at the exploration of the halogen and medium effects on the stability, structural parameters, dipole moment, carbonyl stretching vibration, frontier molecular orbitals, ultraviolet (UV) and density-of-states spectra of the conformers. The atypical characteristics of fluorine and chlorine affecting the electrical-optical band gaps, chemical hardness, partial density-of-states plot, absorption band, and the highest occupied molecular orbital are observed correspondingly. The findings of this research will provide insight for future studies considering conformations analogous to the compounds studied.

INTRODUCTION

The thiophene molecule belongs to a class of heterocyclic compounds containing a five- membered ring made up of one sulfur atom as a heteroatom. This structure can be found in certain natural products and is also incorporated in several pharmacologically active compounds. Thiophene compounds occur rarely in plants and do not play any role in animal metabolism. However, they have found the extensive use in pharmaceuticals and agrochemicals and play some roles in constituents of reactive dyes, conductive polymers, ligands for catalyst systems, and some flavors and fragrances. They also exist in petroleum or coal [1, 2]. Polymers of thiophene or its derivatives are of intense interest in the literature due to their electrical properties and durability [3, 4]. Further, thiophene-containing compounds are well known to exhibit various biological activities such as anti-inflammatory agents [5], anti-HIV or some inhibitors [6, 7], and anti-breast cancer [8].

There are several reports in the literature on changes in the equilibria of conformers with the solvent polarity [9-13]. The conformational preference of the compounds also depends on the variety of substituents [13-16]. In one of our previous studies, we investigated the solvent effects on the conformational isomers of 1,1-dihalogeno-heptan-1-amines, which concluded that the rotational energy barrier was dependent only on the solvent for the F-compound [17].

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In 1979, an *ab initio* molecular orbital study with the STO-3G basis set was conducted by Kao and Radom, considering the conformations, stabilities, and charge distributions in 2- and 3-monosubstituted thiophenes [18]. The stabilizing effect was greater at position 2 than that at position 3. The *cis* form is defined as having the heaviest (generally nonhydrogen) atom of a substituent group *cis* to the ring sulfur atom. For T2C, physical methods such as NMR, IR, and dipole moment measurements suggested that the *cis* conformation was a more stable form in solution. Theoretical results indicated that the *cis* form was also favored over the *trans* one by about 3 kJ/mol in the gas phase [18]. Lunazzi and Placucci measured the interconversion barrier between S,O-*syn*-(*cis*) and S,O-*anti*-(*trans*) conformers of T2C, as 10.15 kcal/mol, by dynamic NMR in 1984 [19]. Similarly, in 1986, a combined electron diffraction and spectroscopic investigation of T2C showed that the major conformer was the one with O and S *syn* [20]. Further, a theoretical study for *syn*- and *anti*- T2C conformers by DFT (B3LYP/6-31G*), normal coordinate and vibrational analyses was reported, and once again the *syn* conformer was found to be more stable than the *anti*-form by 1.36 kcal/mol or 5.6 kJ/mol [21].

In view of the above mentioned literature [9-21] and following our interest in the investigation of solvent or halogen effects on the conformational, vibrational, or electronic properties [9, 17]; this work is aimed to examine the conformational preference, dipole moment, C=O stretching frequency, UV spectrum, frontier orbitals, and density-of-states spectra of the conformers of the title compounds in the gas phase and solutions, using DFT and TDDFT methods in conjunction with B3LYP/6-31++G(d,p). In accordance with this objective, we were interested in revealing the solvent and halogen effects on the conformational isomers and their spectral characteristics.

CALCULATION METHOD

Calculations were carried out by the Gaussian 09 [22] program. All structural and spectroscopic illustrations were made with the GaussView 5.0.8 program [23] and GaussSum 2.2 [24]. The geometrical structures of the conformers of the compounds (Fig. 1), as identified in the previous studies [18-21], were optimized without imposing symmetry, using the B3LYP functional in conjunction with the 6-31++G(d,p) basis set. In order to calculate the barrier of rotation, the transition state for the interconversion was also fully optimized. The ground state structure was confirmed without any negative frequency while the transition state structure had one negative frequency. Further, the PES analysis with B3LYP/6-31++G(d,p) was performed by rotations of the CCCO torsion angle, scanning from 180° to 360° with 20° increments.

Computations were performed in the gas phase and the solvent medium (benzene and methanol) for the compounds. The solvent effect was evaluated by the polarizable continuum model (PCM). The same functional and basis set were used for computing harmonic vibrational frequencies to confirm the nature of the ground state structure. The mole fractions of the
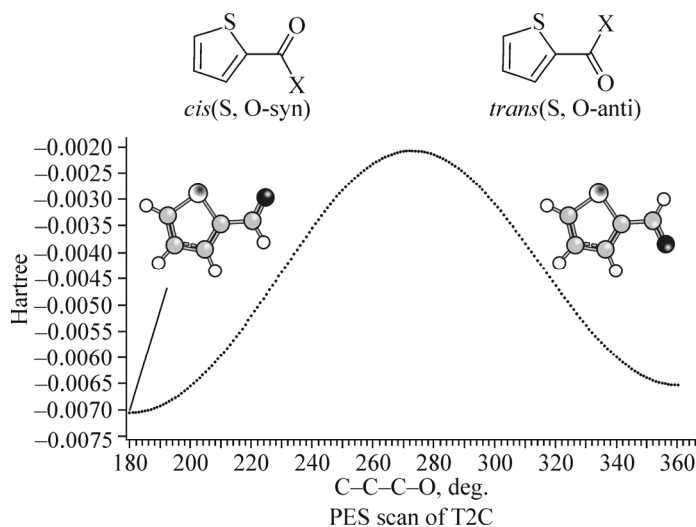

Fig. 1. *Cis* and *trans* conformers of the compounds.

individual conformers were calculated as described previously [17, 25, 26]. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the compounds were analyzed. In order to provide more insights, the electronic properties were also computed by TDDFT [27, 28] based on the optimized structure.

In order to obtain the reliable properties of the molecular orbital expansion, it is essential to employ basis sets of orbitals which possess sufficient diffuseness and angular flexibility [29]. The use of some basis sets in the previous studies for T2C [18, 21] prompted us to optimize these structures using the 6-31++G(*d*,*p*) basis set to gain a deeper insight into the electronic properties.

RESULTS AND DISCUSSION

The outcomes of the electronic computations on the conformers of the compounds are reported and discussed, followed by the analysis of carbonyl stretching frequencies. The electronic properties are also explored.

Conformational analysis. Energy parameters for the optimized structures of the conformers of T2C, T2C-F, T2C-Cl, and T2C-Br in various media are listed in Table 1. As the calculated free energies of T2C in the gas phase show, the *cis* conformer is more stable than *trans* by 1.14 kcal/mol. The computation on the mole fractions of the individual conformers shows that T2C prefers approximately 87% *cis* and 13% *trans* conformations. As can be seen from Fig. 1, the conformational preference is also in agreement with the results obtained from PES by B3LYP/6-31++G(*d*,*p*). The computed free energies in solutions demonstrate that the *cis* conformer appears to be more stable than the *trans* form similarly to the gas phase, with the *cis* form of T2C being 89% in benzene and 92% in methanol. The results of the comparison of these findings are in accordance with the literature [18-21], which conclude that the most stable conformation of T2C does not depend on the medium.

Turning to T2C-F, T2C-Cl, and T2C-Br, in the gas phase, the *cis* conformer is more stable than the *trans* one. When the mole fractions are examined through relative stabilities, it is seen that the *cis* conformation has 55%, 73%, and 78% probabilities respectively. The *cis* conformer is also more stable than the other form for the computed free energies of T2C-F, T2C-Cl, and T2C-Br in solutions. T2C-F, T2C-Cl, T2C-Br in benzene and methanol prefer the *cis* conformer with

TABLE 1. Energy Parameters of the Compounds

Com-pound	Parameter	Gas		Benzene		Methanol	
		trans	*cis*	*trans*	*cis*	*trans*	*cis*
T2C	Free energy, Hartree	−666.3861	−666.3880	−666.3896	−666.3916	−666.3938	−666.3961
	Relative stability, kcal/mol	1.14	0	1.25	0	1.43	0
	Mole fractions, %	13	87	11	89	8	92
	Dipole moment, D	3.6572	4.1216	4.2470	4.7722	5.0043	5.6275
T2C-F	Free energy, Hartree	−765.6887	−765.6889	−765.6921	−765.6923	−765.6961	−765.6963
	Relative stability, kcal/mol	0.12	0	0.13	0	0.16	0
	Mole fractions, %	44	55	45	55	43	57
	Dipole moment, D	4.4881	4.5891	5.1330	5.2456	5.9249	6.0573
T2C-Cl	Free energy, Hartree	−1126.0363	−1126.0372	−1126.0393	−1126.0403	−1126.0431	−1126.0441
	Relative stability, kcal/mol	0.58	0	0.6	0	0.64	0
	Mole fractions, %	27	73	26	74	25	75
	Dipole moment, D	4.4773	4.6025	5.1842	5.3095	6.0794	6.1958
T2C-Br	Free energy, Hartree	−3239.9580	−3239.9592	−3239.9610	−3239.9622	−3239.9648	−3239.9660
	Relative stability, kcal/mol	0.74	0	0.74	0	0.78	0
	Mole fractions, %	22	78	22	78	21	79
	Dipole moment, D	4.5497	4.6690	5.2964	5.4108	6.2687	6.3525

approximate probabilities of 55% and 57%, 74% and 75%, 78% and 79%, respectively. It is observed that the conformational preference is also independent of the halogen.

The free energy barrier of T2C, T2C-F, T2C-Cl, and T2C-Br is 10.88 kcal/mol, 9.75 kcal/mol, 9.56 kcal/mol, and 9.50 kcal/mol, respectively. The result for T2C is in agreement with the experimental interconversion barrier of 10.15 kcal/mol [19]. The optimized energies decrease with the solvent polarity and the halogen size. The mole fraction of the most stable conformer of the compounds gradually increases from the gas phase to the polar solvent. The most stable conformer of T2C-F has the lowest fraction in all media.

The B3LYP/6-31++G(d,p) calculated results in the gas phase show that the dipole moment of the *cis* conformation of T2C is about 4.12 D. This value is in good agreement with the microwave study [30], in which only one conformer was found to be present in the vapor phase with $\mu_a = 3.00$ D and $\mu_b = 1.84$ D. The dipole moment is expected to be larger in solution than that in the gas phase. This is clearly observed in Table 1. In general, it is known that the conformer with a larger dipole moment is less stable. However, the stability of the conformers with larger dipole moments, contradicting the literature data suggesting the rule of larger dipole moments and lower stability, cannot be explained [31].

Some significant changes are found in the geometric parameters when the compounds are solvated. Theoretical bond lengths of the molecules in all media are listed in Table 2. From a lower to higher dielectric, the C=O and C–S bond lengths increase and there are very significant changes in C=O bond lengths of the compounds due to the halogen atom.

ν(C=O) vibrations. In the previous study, the C=O stretching vibrations of the *cis* conformer of T2C in the vapor, matrix, liquid, and crystal were experimentally observed (IR/R) at 1711-1705-1698 cm^{-1}, 1698-1696 cm^{-1}, 1688-1687 cm^{-1}, and 1672-1674 cm^{-1} [20] respectively. It was computed by normal force constant calculations as 1705 cm^{-1} in the same work. Furthermore, this vibration for the *cis* conformer of T2C in the gas phase was theoretically found by some functionals and basis sets [21]. The unscaled values were reported as 1686 cm^{-1}, 1760 cm^{-1}, 1768 cm^{-1}, 1779 cm^{-1}, and 1796 cm^{-1} by BLYP/6-31G(d), B3LYP/6-311G(d,p), SVWN/6-31G(d), B3LYP/6-31G(d), and B3PW91/6-31G(d), respectively, whereas the scaled data were computed at 1676 cm^{-1}, 1704 cm^{-1}, 1738 cm^{-1}, 1710 cm^{-1}, and 1714 cm^{-1}. In the present work, the B3LYP/6-31++G(d,p) predicted values at 1705 cm^{-1} and 1745 cm^{-1}, as scaled [32] and unscaled, for this mode of the *cis* conformer for T2C in the gas phase are in excellent agreement with the experimental data. The C=O stretching frequencies of T2C and its halogen derivatives in various media are collected in Table 3 together with their intensities. The relations between the compounds in the *cis* conformation for various media and their C=O stretching vibrations/intensities are shown in Fig. 2.

As shown in Fig. 2a, the significant changes in the carbonyl stretching modes of the compounds are observed when considering the halogens and solutions. These vibrations of all compounds decrease from the gas phase to methanol. In the gas phase, the frequency increases with the halogen atom, and the F-compound has the highest value. However, in benzene and methanol, these frequencies decrease with halogen, and the F-compound has the lowest data. Similarly to the frequency, in the gas phase, the intensity shows the same trend. The carbonyl stretching intensity increases with the halogen atom, and

TABLE 2. Bond Lengths of the Compounds in Various Media

Com-pound	Bond length, Å	Gas	Benzene	Methanol	Com-pound	Bond length, Å	Gas	Benzene	Methanol
T2C	C=O	1.2136	1.2175	1.2227	T2C-Cl	C=O	1.1901	1.1918	1.1945
	C–S	1.7448	1.7462	1.7484		C–S	1.7499	1.7512	1.7528
	C–C$_{av}$	1.4049	1.4055	1.4045		C–C$_{av.}$	1.4048	1.4040	1.4029
	C–H$_{av}$	1.0885	1.0881	1.0874		C–H$_{av.}$	1.0806	1.0806	1.0805
T2C-F	C=O	1.1884	1.1907	1.1938	T2C-Br	C=O	1.1879	1.1894	1.1916
	C–S	1.7436	1.7448	1.7463		C–S	1.7525	1.7537	1.7552
	C–C$_{av}$	1.4046	1.4038	1.4028		C–C$_{av.}$	1.4042	1.4034	1.4023
	C–H$_{av}$	1.0808	1.0807	1.0806		C–H$_{av.}$	1.0805	1.0805	1.0804

TABLE 3. Carbonyl Stretching of the Compounds in Various Media

Compound	Medium	ν(C=O) unscaled IR, cm^{-1}	ν(C=O) scaled IR, cm^{-1}	IR intensity, km/mol	Compound	Medium	ν(C=O) unscaled IR, cm^{-1}	ν(C=O) scaled IR, cm^{-1}	IR intensity, km/mol
T2C	Gas	1745	1705	390	T2C-Cl	Gas	1823	1741	421
	Benzene	1722	1682	581		Benzene	1721	1681	631
	Methanol	1691	1652	901		Methanol	1690	1651	962
T2C-F	Gas	1860	1776	526	T2C-Br	Gas	1832	1750	415
	Benzene	1720	1680	568		Benzene	1721	1681	662
	Methanol	1689	1650	853		Methanol	1691	1652	1009
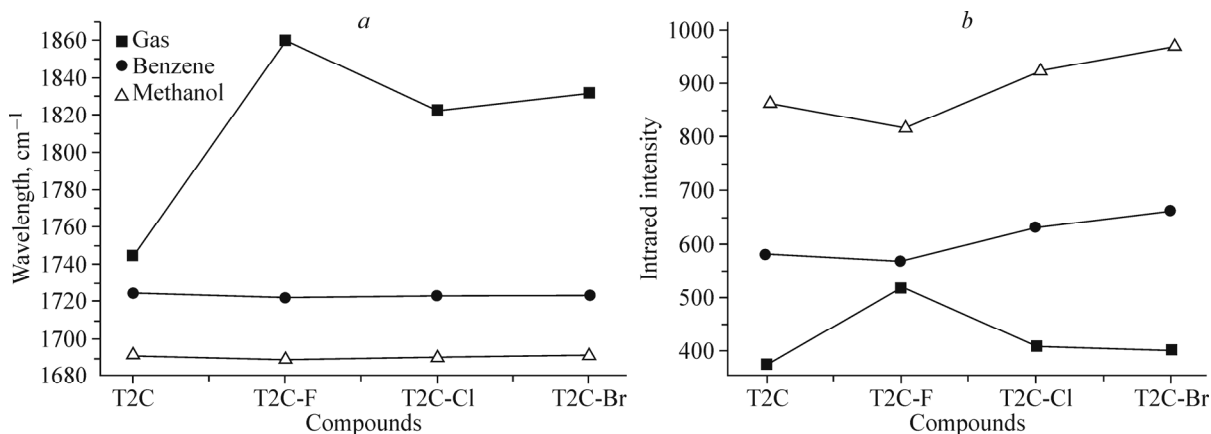
Fig. 2. Plot of the carbonyl stretching frequency (*a*) and intensity (*b*) vs. the compounds.

the F-compound has the highest value. In benzene and methanol, however, these intensities decrease for the F-compound whereas they increase for Cl- and Br-compounds (Fig. 2*b*).

It is necessary to examine the structural parameters of the compounds in various media to have a more comprehensive understanding of the vibrational wavenumbers. The polar medium strongly affects the vibrational frequencies. As seen in Tables 2-3, the C=O bond lengths of the compounds increase on passing from the gas phase to solutions and therefore, ν(C=O) frequencies decrease [9]. The shift can be explained with regard to the increased positive character on oxygen in solutions with high dielectric constants, and hydrogen and halogen bondings [17, 33].

Electronic properties. UV spectra. The UV spectra of the compounds are presented in Fig. 3. Absorption bands are centered at 268.75 nm, 271.16 nm, and 277.54 nm in the gas phase for T2C, T2C-Cl, and T2C-Br, respectively, while it is centered at 259.48 nm for the F-compound. The same trend is observed for the compounds in the solvents. The area of absorption bands increases on passing from the gas phase to the polar solvent. Both halogen and solvent effects on the UV spectra are observed.

The results such as the absorption wavelengths (λ), excitation energies (*E*), and oscillator strengths (*f*) are gathered in Table 4 together with contributions of the transitions. The excitation energies of T2C, T2C-Cl, and T2C-Br in the gas phase are computed as 4.61 eV, 4.57 eV, and 4.46 eV respectively, whereas it is calculated as 4.77 eV for the F-compound. The excitation energy and contribution to the HOMO→LUMO charge transition decreases from a lower to higher dielectric. The transitions, absorption band and optical band gaps depend on the solvent and halogen effects.

Frontier orbitals. HOMO and LUMO energies refer to the ability of electron donating and accepting correspondingly. Hence, the first is directly related to the ionization potential while the latter is related to the electron affinity. The HOMO-LUMO energy difference is known as an electrical band gap. The optical band gap is generally smaller than the electrical one due to the Coulomb interaction. This trend is clearly shown in Tables 4, 5. The energy values of these orbitals
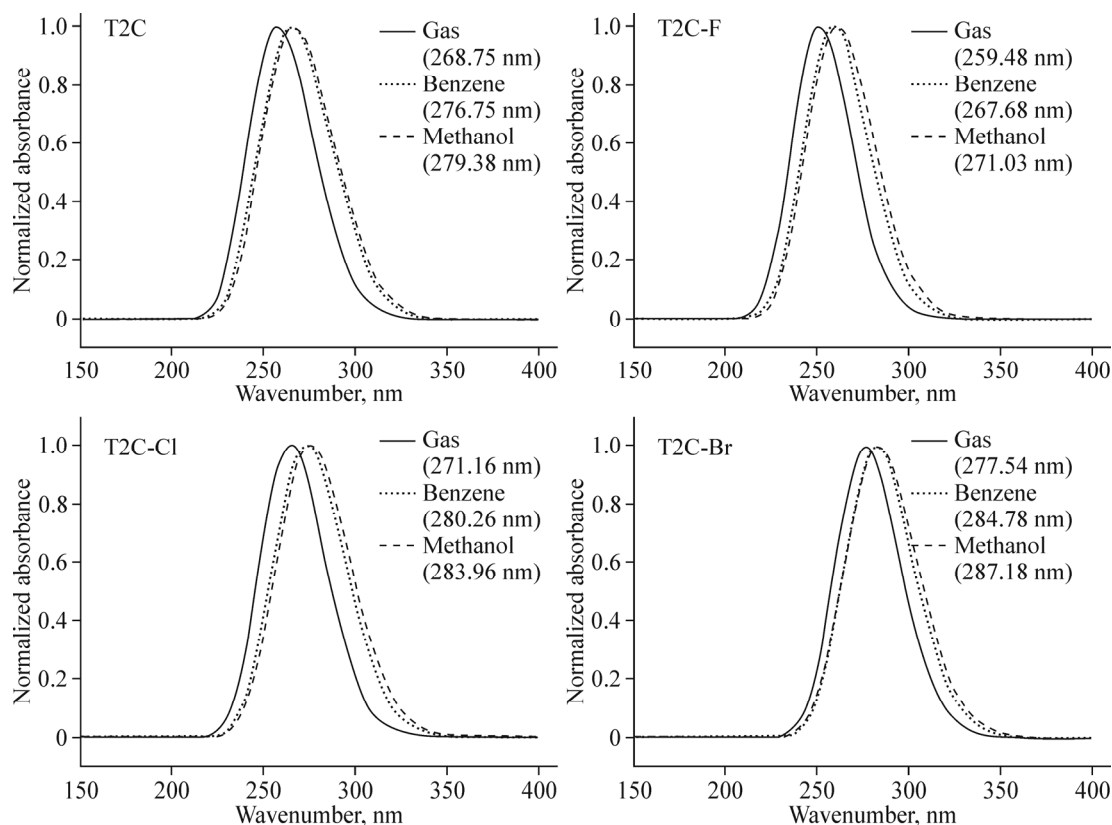
Fig. 3. UV spectra of the compounds.

are presented in Table 5. Electrical band gap energies decrease on passing from the gas phase to the polar solvent for the most stable conformers. The largest HOMO-LUMO gap is observed for the F-compounds in all media (with 5 eV).

The electron donor (HOMO) and electron-acceptor (LUMO) fragments of the compounds in all media are shown in Fig. 4. The contour value of 0.02 is used for the plotting of these diagrams. HOMO is delocalized on almost all atoms of carbaldehyde and thiophene parts for the compounds in the gas phase, whereas it is delocalized on almost all atoms, except C and X atoms of the carbaldehyde group for H-, F-, Br-compounds in the solvents. For the Cl-compound in the solvents, HOMO is localized on the carbaldehyde group. LUMO is delocalized on almost all atoms of the compounds in all media.

The computed data of the chemical hardness, electronegativity, chemical potential, and electrophilicity index are also listed in Table 5. The chemical hardness for T2C, T2C-Cl, and T2C-Br is almost 2.4 eV while for the F-compound, this value is about 2.5 eV, respectively. On passing from the gas phase to the polar solvent, the chemical hardness values of the compounds have a similar trend as the energy gaps. The electronegativity values of T2C-F, T2C-Cl, and T2C-Br also decrease from a lower to higher dielectric. The Br-compound in all media has the largest electronegativity of about 5.1 eV.

DOS diagrams. Partial density-of-states (PDOS) spectra are plotted in Fig. 5. These spectra were plotted by convoluting the molecular orbital information with Gaussian curves of the unit height and full width at half maximum of 0.3 eV. PDOS demonstrate the percentage contribution of a group to each molecular orbital.

According to the PDOS spectra of T2C, HOMO/LUMO for the gas phase and methanol are fairly localized on the carbaldehyde group and with fewer contributions from the thiophene ring while these orbitals in benzene show opposite localization trends. Turning to T2C-F, however, the contribution of the groups is almost equal and there is almost no solvent effect. As for the spectra of T2C-Cl in the gas phase and benzene, the contribution of the carbaldehyde group has the lowest value while the contributions are almost equal for methanol. For T2C-Br in the gas phase, the sequence is the thiophene ring and the carbaldehyde group whereas there is an equal contribution in the solvents. The contributions to frontier orbitals are of the same order for the halogen derivatives. There are both halogen and solvent effects on the partial density of states.

TABLE 4. Calculated Wavelengths, Excitation Energies, and Oscillator Strengths of the Compounds

Compound	Medium	E, eV	λ, nm	f	Contribution
T2C	Gas	3.67	338.06	0.0002	H-1→L (97%), H-1→L+2 (3%)
		4.61	268.75	0.1364	H→L (64%), H-2→L (33%),
		4.93	251.36	0.1935	H-2→L (63%), H→L (33%)
	Benzene	3.72	332.73	0.0002	H-1→L (97%), H-1→L+2 (3%)
		4.48	276.75	0.2046	H→L (73%), H-2→L (24%),
		4.80	258.38	0.2390	H-2→L (72%), H→L (25%)
	Methanol	3.80	325.88	0.0002	H-2→L (97%), H-2→L+2 (2%)
		4.43	279.38	0.1760	H→L (68%), H-1→L (30%)
		4.77	260.00	0.2483	H-1→L (67%), H→L (30%)
T2C-F	Gas	4.77	259.48	0.1501	H→L (66%), H-1→L (30%)
		5.06	245.04	0.1777	H-1→L (65%), H→L (31%)
		5.08	244.12	0.0000	H-2→L (96%), H-2→L+3 (2%)
	Benzene	4.63	267.68	0.2106	H→L (74%), H-1→L (23%)
		4.92	251.94	0.2274	H-1→L (73%), H→L (24%)
		5.17	239.85	0.0000	H-2→L (97%), H-2→L+3 (2%)
	Methanol	4.57	271.03	0.1862	H→L (70%), H-1→L (27%)
		4.88	254.12	0.2331	H-1→L (70%), H→L (27%)
		5.27	235.06	0.0000	H-2→L (97%), H→L (27%)
T2C-Cl	Gas	4.42	280.10	0.0001	H-2→L (95%), H-4→L (2%)
		4.57	271.16	0.1810	H→L (70%), H-1→L (26%)
		4.82	257.21	0.1548	H-1→L (70%), H→L (25%)
	Benzene	4.42	280.26	0.2581	H→L (78%), H-1→L (19%)
		4.49	275.78	0.0001	H-2→L (95%), H-4→L (2%)
		4.69	264.12	0.1927	H-1→L (78%), H→L (19%)
	Methanol	4.36	283.96	0.2195	H→L (74%), H-1→L (24%)
		4.58	270.72	0.0001	H-2→L (95%), H-4→L (2%)
		4.63	266.68	0.2140	H-1→L (73%), H→L (23%)
T2C-Br	Gas	4.11	301.35	0.0001	H-4→L (12%), H-2→L (86%)
		4.46	277.54	0.2181	H→L (81%), H-3→L (16%)
		4.60	269.10	0.0213	H-1→L (88%), H-3→L (7%)
	Benzene	4.18	296.46	0.0001	H-4→L (11%), H-2→L (86%)
		4.35	284.78	0.3279	H→L (87%), H-3→L (5%), H-1→L (6%)
		4.55	272.53	0.0503	H-1→L (86%), H-3→L (8%), H→L (3%)
	Methanol	4.26	290.69	0.0002	H-4→L (11%), H-2→L (87%)
		4.31	287.18	0.2795	H→L (81%), H-1→L (14%), H-3→L (2%)
		4.53	273.77	0.1094	H-1→L (80%), H→L (11%), H-3→L (7%)

H and L denote HOMO and LUMO, respectively.

TABLE 5. Energy (eV) for the Frontier Orbitals and Some Parameters of the Compounds

Compound	Medium	HOMO	LUMO	Gap	Chemical hardness (h)	Electro-negativity (χ)	Chemical potential (μ)	Electrophilicity index (ω)
T2C	Gas	−7.259	−2.325	4.934	2.467	4.792	−4.792	4.655
	Benzene	−7.217	−2.331	4.885	2.442	4.774	−4.774	4.666
	Methanol	−7.196	−2.369	4.827	2.413	4.783	−4.783	4.739
T2C-F	Gas	−7.577	−2.462	5.116	2.558	5.019	−5.019	4.925
	Benzene	−7.497	−2.441	5.056	2.528	4.969	−4.969	4.884
	Methanol	−7.427	−2.444	4.983	2.491	4.935	−4.935	4.888
T2C-Cl	Gas	−7.596	−2.659	4.936	2.468	5.127	−5.127	5.326
	Benzene	−7.517	−2.643	4.873	2.437	5.080	−5.080	5.295
	Methanol	−7.445	−2.650	4.795	2.398	5.047	−5.047	5.313
T2C-Br	Gas	−7.599	−2.720	4.880	2.440	5.159	−5.159	5.455
	Benzene	−7.525	−2.697	4.827	2.414	5.111	−5.111	5.411
	Methanol	−7.457	−2.699	4.758	2.379	5.078	−5.078	5.419
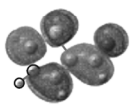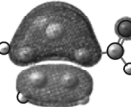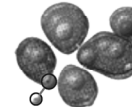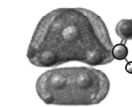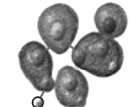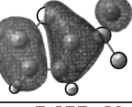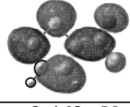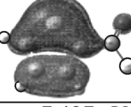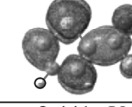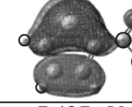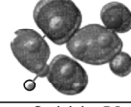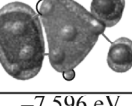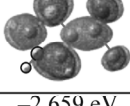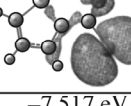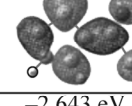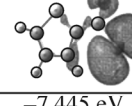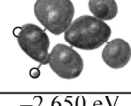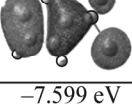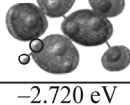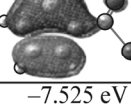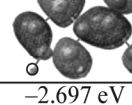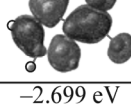
Compound	Gas		Benzene		Methanol	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
T2C						
	−7.259 eV	−2.325 eV	−7.217 eV	−2.331 eV	−7.196 eV	−2.369 eV
T2C-F						
	−7.577 eV	−2.462 eV	−7.497 eV	−2.441 eV	−7.427 eV	−2.444 eV
T2C-Cl						
	−7.596 eV	−2.659 eV	−7.517 eV	−2.643 eV	−7.445 eV	−2.650 eV
T2C-Br						
	−7.599 eV	−2.720 eV	−7.525 eV	−2.697 eV	−7.457 eV	−2.699 eV

Fig. 4. Frontier molecular orbitals of the compounds.

CONCLUSIONS

To explore the solvent and halogen effects on the conformational, vibrational, and electronic characteristics of T2C, T2C-F, T2C-Cl, and T2C-Br, a theoretical DFT and TDDFT study has been undertaken. To summarize, the salient features of this research are:

1. The conformations are stabilized when the solvent polarity and the halogen size increase.

2. The conformational energy barrier does not depend on the solvent and halogen effects.

3. The lowest mole fraction in all media belongs to the F-compound.

4. An increase in the basis set and a change in the functional do not affect the most stable form.
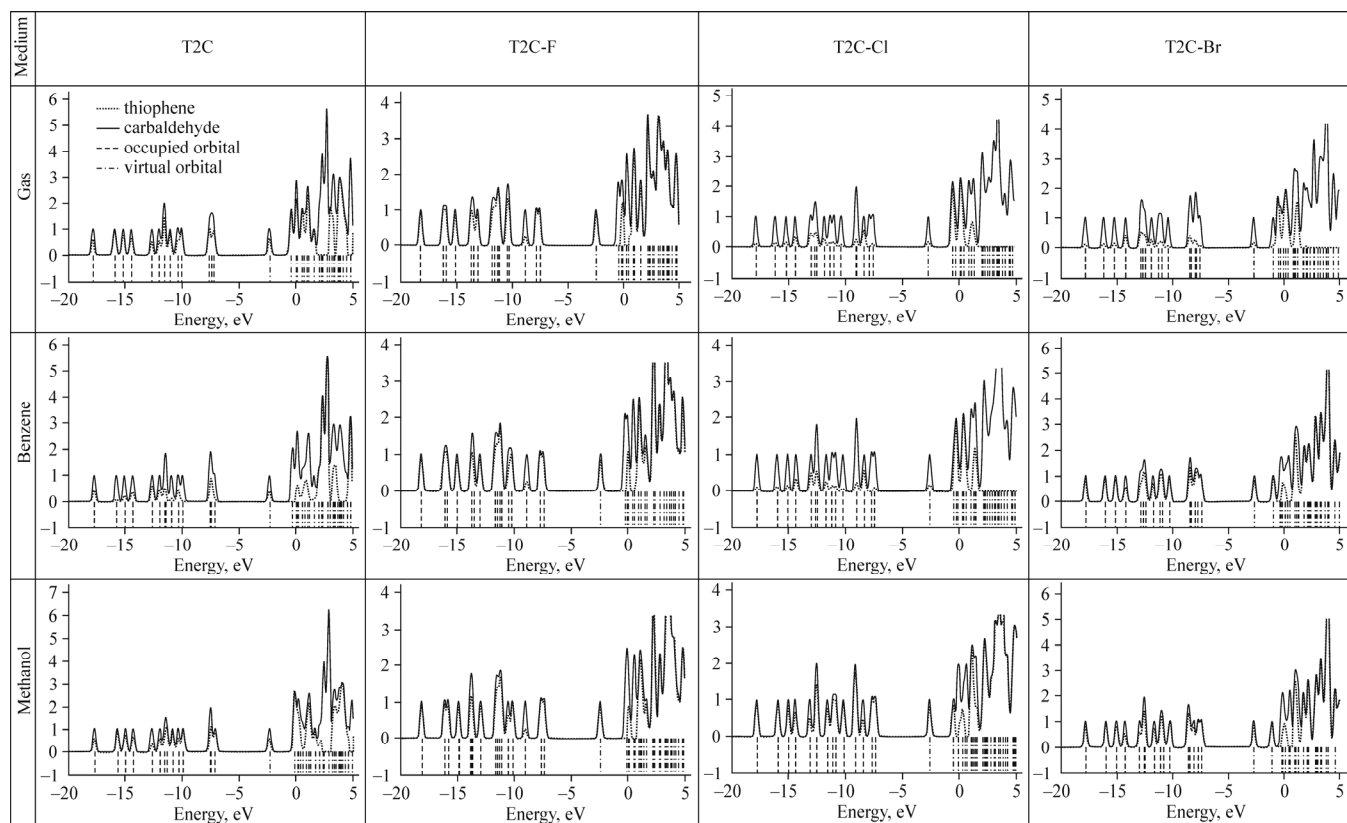
Fig. 5. PDOS spectra of the compounds.

5. There are high interconversion energy barriers. The energy barrier of T2C is about 10.9 kcal/mol. Although the energy difference between the conformers for the halogen derivatives is less than 0.7 kcal/mol; the barrier also is at least 9.5 kcal/mol.

6. It is worth noting that the compounds have large dipole moments (at least 4 D) and this is an essential criterion for the drug-receptor interaction [34].

7. The C=O stretching vibrations of all compounds decrease from the gas phase to methanol whereas their intensities increase.

8. The F-compound has the highest frequency or intensity in the gas phase while it has the lowest values in solutions.

9. The electrical band gap for the compounds in all media is greater than 4.7 eV, which is sufficiently large to meet the viability criterion suggested by Hoffmann et al. [35].

10. Fluorine has an atypical characteristic affecting the electrical and optical band gaps, chemical hardness, PDOS plot, and absorption band whereas chlorine has an atypical feature influencing the HOMO level.

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