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Effects of Rotational Isomerism and Bond Length Alternation on Optical Spectra of FTC Chromophore in Solution

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Rotational isomerism effects on the optical spectra of a push-pull nonlinear optical chromophore 2-dicyanomethylen-3-cyano-4-{2-[*E*-(4-*N,N*-di(2-acetoxyethyl)-amino)-phenylene-(3,4-dibutyl)-thien-5]-*E*-vinyl}-5,5-dimethyl-2,5-dihydrofuran (FTC) in a few solvents have been studied using the time-dependent density functional theory in combination with the polarizable continuum model. It is shown that the maximum absorption peaks of the rotamers have difference of nearly 30 nm both in vacuum and in solutions. The population of the rotamers changes a lot in different solvents. Based on the geometries optimized by Hartree-Fock method, the Maxwell-Boltzmann averaged absorption has been calculated and the maximum absorption peak is in good agreement with experiment. It indicates that the bond length alternation can have an important effect on the optical spectra.

Key words: Rotational isomerism, Bond length alternation, One-photon absorption, Polarizable continuum model

I. INTRODUCTION

Organic chromophores possessing a high degree of π -conjugation have become one of the most important candidates for nonlinear optical (NLO) materials [1–3]. Extensive research has been carried out to explore the so-called structure-to-property relationships at the molecular level [1, 3–5]. The accurate calculations of one-photon absorption (OPA) properties not only provide the assessment of various computational methods [6, 7] compared with experimental results, but also are the prerequisite for the further study of NLO properties, such as the first-order hyperpolarizability and two-photon absorption (TPA) [8, 9].

It is well known that the linear absorption spectra of charge-transfer conjugated molecules may be influenced by the surrounding medium, and solvents can bring about a change in the position, intensity, and even the shape of absorption bands, which is termed as solvatochromism [10]. A large number of solvatochromic behaviors have been observed for many organic chromophores with strong NLO responses [10, 11]. The significant modifications of the spectra can be understood from the changes in the geometries and electronic structures of the solute molecule due to the intermolecular interactions in condensed phase. It has been demonstrated that some important conformational parameters including the bond length alternation (BLA) [12], the main torsional/dihedral angles [13, 14], and the orien-

tations of branches [15, 16] are responsible for the solvent effects on linear and nonlinear optical properties. In some cases, the solvatochromic behaviors can be attributed to the electronic structures such as ground and excited state dipole moments [17].

Recently, the influence of isomerism on optical properties has been investigated [7, 18–24]. We have analyzed the isomer dependence of optical absorptions on a V-shaped hydroxypyrimidine molecule in tetrahydrofuran and chloroform solutions at length [19]. It was shown that the experimentally observed large spectral shift in OPA and large enhancement in TPA cross sections in different solutions can be well interpreted by the involvement of molecular isomers. Guillaume and coworkers studied the effects of conformational averaging on OPA, TPA and circular dichroism [23]. The comparison between the Maxwell-Boltzmann (MB) weighted spectra and experimental linear spectroscopy turned out to be rather satisfactory. In the work of Nguyen *et al.*, the computed OPA spectrum obtained by Boltzmann average over multiple low-lying isomers gets better agreement with experimental observations than that of the lowest-energy conformer [24].

It is expected that many flexible conjugated molecules with single bonds have thermal populations of rotational isomers (rotamers) [22]. The 2-dicyanomethylen-3-cyano-4-{2-[*E*-(4-*N,N*-di(2-acetoxyethyl)-amino)-phenylene-(3,4-dibutyl)-thien-5]-*E*-vinyl}-5,5-dimethyl-2,5-dihydrofuran (FTC) chromophore is a candidate flexible molecule and has been well-studied [7, 21, 22, 25]. This push-pull chromophore exhibits nice NLO properties, characterized by a large hyperpolarizability. Kinnibrugh *et al.* have explored

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the influence of rotational and geometrical isomerism on the first-order hyperpolarizability of FTC with density functional theory (DFT) [22]. Their calculations indicates that the conformational energies of the manifold of rotamers are near degenerate and the rotational average should not be ignored. The effect of the conformational space on the ultraviolet-visible (UV-Vis) spectra has been taken into account by Andzelm *et al.* [7]. However, they calculated the absorption spectra only in gas phase and in cyclohexanone solution. Other polar solvents have not been considered. Furthermore, the effects of some important structural parameters such as the bond distance or the BLA have not been explored.

In order to further study the influence of the solvent reaction field on rotameric populations and on the OPA properties, in this work, we perform a systematic investigation of the geometries and electronic structures for FTC rotamers in vacuum and in solvents with increasing polarity: chloroform, cyclohexanone, methanol and water. The MB weights for these rotamers in vacuum and in solutions are obtained. The OPA spectra and oscillator strengths are calculated using time-dependent DFT (TD-DFT) approach in combination with the polarizable continuum model (PCM). Also, from the geometrical point of view, we put forward a possible explanation of the experimental observations. This work also specifies how OPA properties are influenced by the rotamers in various solutions and explores the relationships of structure and optical properties.

II. COMPUTATIONAL METHODS

The transition probability of OPA is conventionally given by oscillator strength [26]:

$$\sigma = \frac{2\omega_f}{3} \sum_{\alpha} |\langle 0 | \mu_{\alpha} | f \rangle|^2 \quad (1)$$

where μ is the electric dipole moment operator, ω_f denotes the excitation energy from the ground $|0\rangle$ to the excited $|f\rangle$ states, and the summation is performed over the molecular axes: $\alpha \in (x, y, z)$.

According to Boltzmann distributions, the probability of each molecular conformation with energy E_{α} at temperature T can be described by the corresponding MB weight X which is expressed as

$$X = \frac{\exp[-(E_{\alpha}/k_{\text{B}}T)]}{\sum_{\alpha} \exp[-(E_{\alpha}/k_{\text{B}}T)]} \quad (2)$$

where k_{B} is the Boltzmann's constant and the summation runs over all possible conformers.

All the calculations are implemented in Gaussian 03 [27] program. The geometry optimizations in the gas phase and in solutions are carried out with the 6-31G(d,p) basis set at the Hartree-Fock (HF) and B3LYP levels of theory [7]. The 6-31+G(d,p) basis set

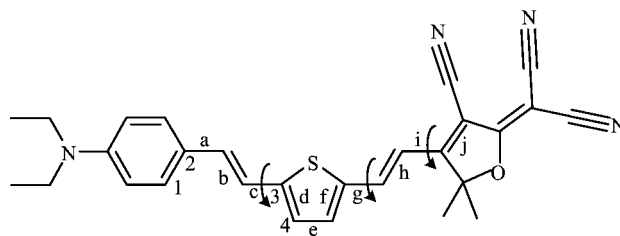


FIG. 1 The chemical formula of FTC chromophore.

is used to obtain the single point energies on optimized geometries. To estimate the vertical excitation energies and the corresponding oscillator strengths, we have used the TD-DFT approach with B3LYP functional at 6-31G(d,p) basis set. The solvent effect is considered by means of the PCM [28]. The use of larger basis sets could probably provide better numerical results, but we believe that the overall picture would not change.

III. RESULTS AND DISCUSSION

A. Rotational isomerism

The chemical formula of FTC molecule is presented in Fig.1. FTC molecules has three significant single bonds (labeled as c, g, and i here) along the conjugated backbone which can give rise to a manifold of rotamers [21, 22]. With different initial conformations, the most probable rotamers are fully optimized in vacuum and in different solvents at the B3LYP level. The calculations indicate that the geometries of each rotamer look almost the same in all the phases. Thus, as an example, the convergent geometries of rotamers in chloroform are exhibited in Fig.2. For each of the rotatable single bonds, two rotational states located near 0° and 180° are denoted by *transoid* (*trans*) and *cisoid* (*cis*), as these states bring the double bonds adjacent to the rotatable bond into *trans* and *cis* orientations relative to another [22]. The names of other rotamers are all defined according to the following rules. For example, the first letter "t" in the name of "ttc" means the double bonds of b and d are on the other side of the single bond c, the second letter "t" denotes the double bonds of f and h are also on the other side of the single bond g, and the last one "c" refers to the double bonds h and j are on the same side of the bond i. It is noticed that these rotamers have different structural features. It is easy to see that conformers cct and ccc each have a nearly linear backbone, while the conformer ttt has a considerable angle between the branch with benzene and the one with furan ring. Such a different conjugation could lead to different absorption properties. It is also noticed that the rotation around bond i at the furan ring could bring about different strengths of acceptor groups.

For conjugated molecules, one of the most important geometric parameters is the BLA which is defined as the

TABLE I Bond length alternations (BLA) and permanent dipole moments μ of the rotamers in vacuum and in solutions.

Rotamer	Vacuum		Chloroform		Cyclohexanone		Methanol		Water	
	BLA/Å	μ/D	BLA/Å	μ/D	BLA/Å	μ/D	BLA/Å	μ/D	BLA/Å	μ/D
ttc	0.0420	22.76	0.0262	31.85	0.0244	33.46	0.0186	35.83	0.0178	36.31
ttt	0.0430	20.31	0.0280	28.46	0.0265	29.86	0.0208	32.05	0.0206	32.66
ctc	0.0411	23.12	0.0244	32.54	0.0222	34.23	0.0162	36.69	0.0153	37.16
ctt	0.0426	21.65	0.0264	30.72	0.0246	32.33	0.0189	34.74	0.0181	35.43
tct	0.0440	22.88	0.0290	32.17	0.0272	33.77	0.0216	36.20	0.0211	36.70
tcc	0.0411	20.72	0.0257	29.20	0.0242	30.60	0.0188	32.89	0.0176	33.48
cct	0.0429	23.04	0.0269	32.46	0.0249	34.10	0.0190	36.66	0.0184	37.16
ccc	0.0404	21.84	0.0244	30.94	0.0222	32.68	0.0164	35.13	0.0156	35.68

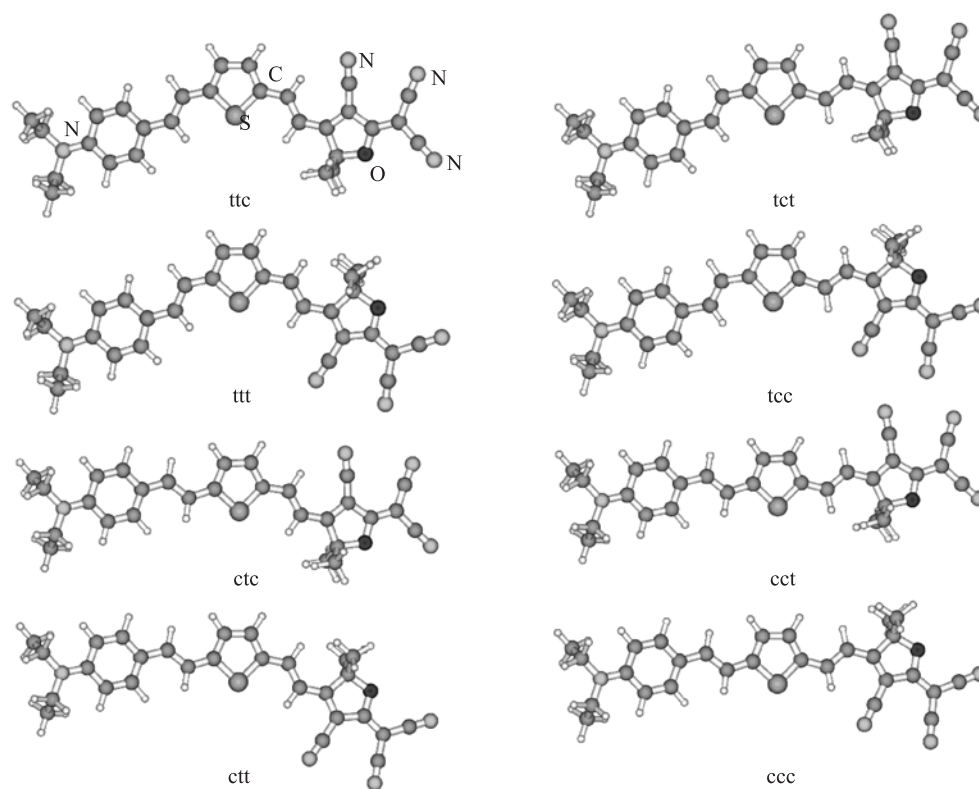


FIG. 2 Optimized structures of the rotamers in chloroform.

difference in length between the single and double bonds [12, 29]. In order to examine the geometrical changes of the rotamers in selected solutions, we calculated the BLA, and the values are collected in Table I. The BLA parameter for FTC molecule is determined by [30]:

$$\text{BLA} = \frac{1}{4} \left[\frac{1}{2} (a + i) + c + e + g - b - d - f - h \right] \quad (3)$$

where the bonds represent bond length, indicated in Fig.1. The results show that for different conformers the BLA values have little difference in the same environment. The BLA is found to be about 0.04 Å in

vacuum for all the rotamers. However, with increasing solvent polarity, the BLA values are decreased obviously. For instance, in water, the BLA of rotamer ttc is 0.0178 Å, which is much smaller than the corresponding value of 0.0420 Å in vacuum. This indicates that the solvent effects on the molecular geometry are significant. Similar behavior has been seen in other push-pull molecules [12, 31]. As electronic structures are closely related to optical properties, the permanent dipole moments of the ground states for all the rotamers are also shown in Table I. In contrast to the case of BLA, in the same environment, the permanent dipole moments of the eight rotamers are noticeably different. In all the cases,

TABLE II Energy differences ΔE (in kcal/mol) and MB weights X of the rotamers in vacuum and in solutions.

Rotamer	Vacuum		Chloroform		Cyclohexanone		Methanol		Water	
	ΔE	$X/\%$	ΔE	$X/\%$	ΔE	$X/\%$	ΔE	$X/\%$	ΔE	$X/\%$
ttc	0.00	50.76	0.13	31.65	0.25	27.16	0.47	19.91	0.57	17.02
ttt	0.34	28.27	0.00	39.57	0.00	41.74	0.00	44.05	0.00	45.33
ctc	0.88	11.17	0.74	11.09	0.83	10.02	0.92	9.30	0.96	8.70
ctt	1.43	4.37	0.70	11.88	0.65	13.66	0.49	19.25	0.46	20.56
tct	1.72	2.64	1.55	2.76	1.45	3.45	1.56	3.17	1.43	3.88
tcc	1.98	1.68	1.86	1.62	1.80	1.89	1.85	1.94	1.98	1.51
cct	2.47	0.71	2.20	0.90	2.01	1.32	2.03	1.41	1.80	2.05
ccc	2.83	0.40	2.51	0.53	2.34	0.75	2.26	0.97	2.25	0.95

TABLE III Calculated OPA wavelengths λ_{\max} and corresponding oscillator strengths f of the rotamers in vacuum and in solutions.

Rotamer	Vacuum		Chloroform		Cyclohexanone		Methanol		Water	
	λ_{\max}/nm	f	λ_{\max}/nm	f	λ_{\max}/nm	f	λ_{\max}/nm	f	λ_{\max}/nm	f
ttc	608	1.61	701	1.93	708	1.94	700	1.98	701	2.00
ttt	617	1.40	707	1.73	710	1.76	704	1.79	704	1.81
ctc	595	1.81	682	2.13	692	2.15	684	2.19	685	2.21
ctt	600	1.64	690	2.01	693	2.05	687	2.08	687	2.10
tct	619	1.64	713	2.03	718	2.05	711	2.09	712	2.10
tcc	624	1.51	715	1.87	720	1.90	711	1.94	713	1.96
cct	605	1.75	697	2.15	700	2.17	694	2.22	695	2.23
ccc	607	1.69	697	2.06	702	2.10	693	2.14	694	2.15
Average	609	1.57	700	1.89	706	1.91	698	1.94	699	1.96

the rotamer ctc has the largest dipole moment and the conformer ttt has the smallest one due to the lack of linear backbone. The differences between the maxima and the minima are computed to be 2.81 D in vacuum, 4.08 D in chloroform, 4.37 D in cyclohexanone, 4.64 D in methanol, and 4.5 D in water, respectively. An interesting observation is that the dipole moments of these isomeric species increase in a consistent manner with increasing polarity of the solvent. The reason is that a polar solvent polarizes a solute more significantly than a nonpolar solvent and hence induces a larger charge separation which results in a higher dipole moment.

The single point energies on the optimized geometries in vacuum and in different solutions are calculated using bigger basis set 6-31+G(d,p) at the B3LYP level and the obtained energy differences with respect to the lowest energy, as well as the corresponding MB weights at room temperature are given in Table II. In vacuum, it is found that the ttc has the lowest energy among these rotamers and the energy differences between other structures and ttc are very small in general. For the ttt and ctc, the energy differences are only 0.34 and 0.88 kcal/mol, respectively. The MB weights X demonstrate that the conformers with small energy difference can be populated at certain percentages such as 28.27% for ttt

and 11.17% for ctc. The lowest-energy conformer ttc only takes up to 50.76%. As expected, the presence of solvent makes an important change in the order of energy. In all the solutions, the lowest-energy conformer is replaced by the rotamer ttt. Moreover, the population of ttt is enhanced with increasing solvent polarity, while the component of ttc is found to be decreased. In water, the percentage of ttc is only 17.02%, even lower than that of the ctt (20.56%). This indicates that the orientation of furan ring in ttt is more advantageous to the molecular stability than that in ttc in more polar solvents. It is interesting to observe that the population of the ctt, similar to the ttt and ttc, is also changed significantly from vacuum to water, which makes the ctt become an important component in water. In addition, it is noticed that the energy differences of these rotamers still remain small in all the solutions.

The experimental linear absorption spectrum of FTC chromophore in cyclohexanone solvent is composed of two major bands centered at 650 and 400 nm [25] which correspond to the intramolecular charge transfer (CT) and the local excitation. The CT state produces the maximum absorption peak (λ_{\max}), while the local transition has a much lower oscillator strength. In Table III, we present the results of our TD-DFT calculations for

TABLE IV Main bond distances $a-i$, BLA, dihedral angle θ , and permanent dipole moments μ of ttt rotamer optimized at the HF and the B3LYP levels in vacuum and in cyclohexanone.

		Bond distance/Å								BLA/Å	$\theta/(^\circ)$	μ/D	
		a	b	c	d	e	f	g	h				i
Vacuum	HF	1.4682	1.3310	1.4581	1.3589	1.4204	1.3575	1.4454	1.3387	1.4467	0.0988	12.97	16.51
	B3LYP	1.4469	1.3601	1.4336	1.3940	1.4013	1.3927	1.4211	1.3711	1.4208	0.0430	3.77	20.31
Cyclohexanone	HF	1.4688	1.3320	1.4583	1.3598	1.4200	1.3591	1.4408	1.3431	1.4380	0.0947	5.85	21.47
	B3LYP	1.4400	1.3661	1.4270	1.4011	1.3943	1.3999	1.4095	1.3815	1.4077	0.0265	0.65	29.86

the CT states in vacuum and in various solutions. The geometries of the rotamers have been optimized in solvents by the PCM method and the B3LYP functional at the 6-31G(d,p) basis set was used in the calculations. First, it is found that the eight rotamers have different absorption properties both in vacuum and in solutions. The absorption maximum λ_{\max} in vacuum is changed from 595 nm of ctc to 624 nm of tcc. The shift nearly comes to be 30 nm. In all the solutions, the λ_{\max} peak difference between ctc and tcc is still about 30 nm. Secondly, the statistical averages of the peaks are not exactly equal to the values of the lowest-energy conformer, but the deviation is less than 7 nm. In chloroform, the average λ_{\max} is equal to 700 nm, blue-shifted by 7 nm with respect to the λ_{\max} of ttt. This is because ttc, ctc and ctt have considerable populations in this case, as shown in Table II. With the increasing population of ttt, the average λ_{\max} becomes closer to the one of ttt. Although the populations of these rotamers changes a lot in various solutions, the averaged absorption peak positions are almost the same in different solvents. Thirdly, all the conformers exhibit large positive solvatochromism and the behavior of the absorption maximum as a function of dielectric constant of the solvent is non-monotonic. For example, λ_{\max} of ttc shifts from 608 nm to 701 nm on going from the gas phase to chloroform and the maximum value of λ_{\max} for ttc occurs in cyclohexanone. It is also noticed that the oscillator strength is enhanced upon solvation. At last, the calculated absorption maximum with the B3LYP geometry is not in agreement with experimental results. The deviation comes to be 56 nm in cyclohexanone.

B. Bond length alternation

As well known, the accuracy of results depends strongly on the applied methods. Andzelm *et al.* have assessed the efficiency of several DFT functionals for reproducing the experimental absorption wavelength based on the B3LYP optimized structures [7], and concluded the hybrid functionals B3LYP and PBE0 as well as BNL with the attenuation parameter $\gamma=0.1$ and CAM-B3LYP with $\gamma=0.05$ would yield the λ_{\max} -transition within the target accuracy of 30 nm. From a

different point of view, the optical properties also highly depend on the used geometries. Even the most accurate electronic structure method will fail if the molecular geometry is inaccurate. It has been known that the electron density described by B3LYP is more localized, resulting in a larger charge separation in the charge-transfer molecule [32]. Early studies on the similar systems have also shown that the HF method is superior to the B3LYP approach in correct predicting the BLA parameter [33]. Therefore, we have optimized the geometry of ttt, as an example, both at the B3LYP and the HF levels with the 6-31G(d,p) basis set in vacuum and in cyclohexanone.

The main structural parameters of ttt, along with the permanent dipole moment of the ground state are presented in Table IV. The dihedral angle θ is defined by the four C atoms which are labeled with numbers in Fig.1. It should be mentioned that the thiophene and furan ring are nearly coplanar in two methods and so the dihedral angle between them is not discussed here. From Table IV, one can see that the B3LYP geometry tends to give a longer conjugation length, a shorter BLA value, a better planarity, and a larger dipole moment with respect to the HF geometry. The BLA values of the HF geometries are 0.0988 Å in vacuum and 0.0947 Å in cyclohexanone, which are much larger than those of the corresponding B3LYP geometries. The HF geometry has a nonplanar structure in vacuum with $\theta=12.97^\circ$ and θ is decreased to 5.85° on going from the gas phase to cyclohexanone solution.

In order to investigate the OPA dependence on the dihedral angle, we have carried out a set of constrained geometry optimizations in the gas phase for different dihedral angles at the HF level. For each of constrained geometries, the excitation energies have been obtained at the B3LYP level in combination with the PCM. The conformation energy difference and the OPA wavelength shift with respect to the relaxed geometry as functions of dihedral angle are illustrated in Fig.3. It is noted that a significant deviation (90°) from the equilibrium geometry only requires 2.18 kcal/mol. This demonstrates that the change of dihedral angle is possible from the thermodynamic point of view. The OPA wavelength is blue-shifted with the increase of θ and the maximum shift is 23 nm. Such results suggest that

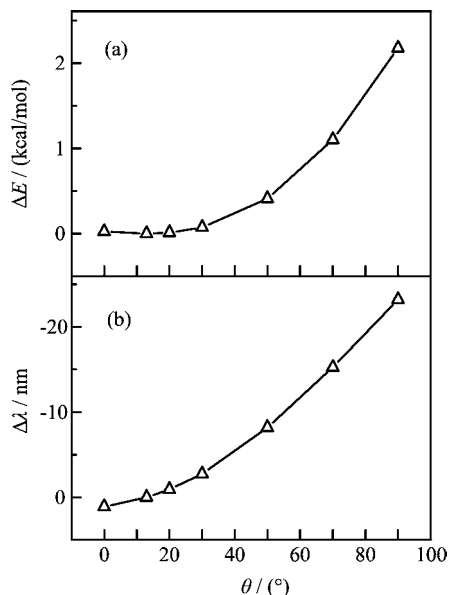


FIG. 3 (a) Conformation energy difference ΔE and (b) OPA wavelength shift $\Delta\lambda$ as functions of dihedral angle θ .

the torsion of the backbone does not play an important role in the OPA peak position. To further confirm this finding, we also performed similar constrained optimizations by manual rotating the bond c, g, and i, respectively. The changes of the OPA wavelength are still within 30 nm in all the cases.

Finally, all the rotamers are optimized without constraints at the HF level and the corresponding excitation energies and the oscillator strengths are calculated at the B3LYP level in cyclohexanone solution. The results are displayed in Table V. In comparison with the B3LYP geometries, the order of energy is unchanged. The λ_{\max} has a 27 nm shift between tcc and ctt. The most important observation is that the λ_{\max} peaks of these rotamers are located in the vicinity of 650 nm and then the averaged λ_{\max} is consistent with experimental value very well. Since the change of torsional angle can not bring about a large wavelength shift, as analyzed above, it is reasonable to speculate that the improvement of calculated maximum absorption position mainly results from the bond distances or the BLA parameter which are obtained by HF method.

IV. CONCLUSION

The absorption spectra of FTC rotamers in several solvents have been investigated employing the TD-DFT in combination with the PCM method. The effects of rotational isomerism on structures and absorption properties are discussed in detail. It is found that the absorption properties of the rotamers are different both in vacuum and in solutions. The maximum absorption peak position has a nearly 30 nm shift among these rotamers in all cases. It is also shown that the presence of

TABLE V Energy differences ΔE , MB weights X , and the calculated OPA wavelengths λ_{\max} and the oscillator strengths f of the rotamers optimized at the HF level in cyclohexanone.

Rotamer	ΔE /(kcal/mol)	X /%	λ_{\max} /nm	f
ttc	0.21	33.64	657	1.17
ttt	0.00	48.23	652	1.05
ctc	1.23	6.03	646	1.25
ctt	1.07	7.96	640	1.11
tct	1.77	2.44	657	1.20
tcc	2.27	1.05	667	1.13
cct	2.77	0.44	645	1.15
ccc	3.23	0.21	654	1.14
Average			653	1.11

solvent changes the order of energy and the corresponding populations of the rotamers. From the geometrical point of view, we have optimized the geometries of rotamers using HF method and the averaged maximum absorption wavelength is in a good agreement with the experimental value. Our calculations indicate that the BLA parameter can give rise to an important effect on the OPA property of FTC chromophore.

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