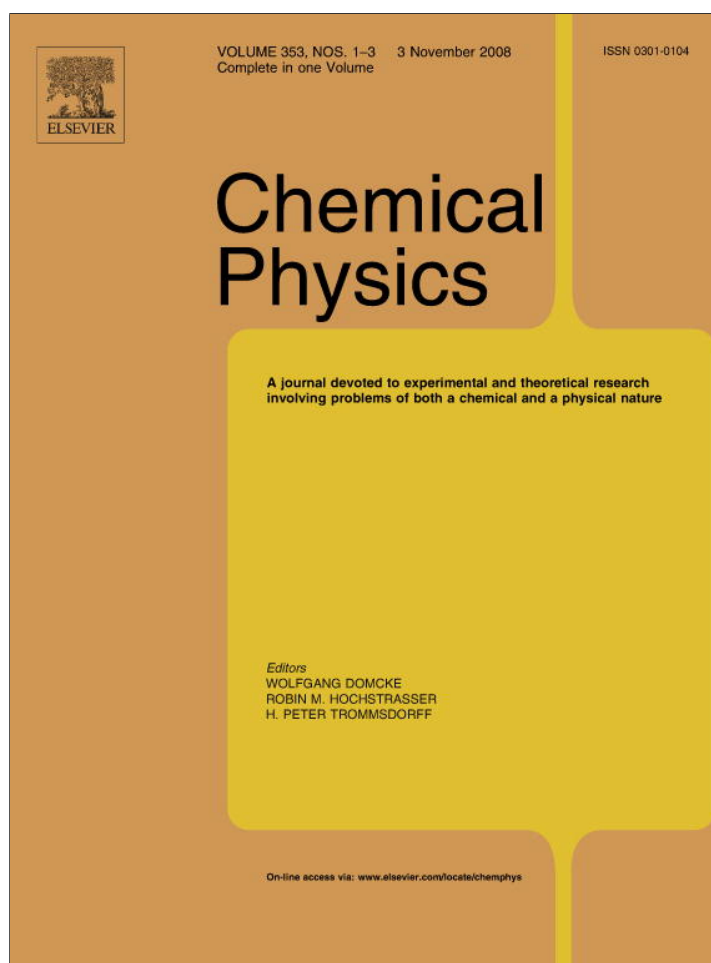




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Structures, spectra and photophysics of new organic fluorophores: 2,3- and 2,5-di(phenylethenyl)furan

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ABSTRACT

The rotational isomerism, electronic structure and photophysics of two new organic fluorophores, the 2,3- and 2,5-di(phenylethenyl)furan have been studied by a combined theoretical and experimental approach. The conformers of the ground electronic state have been investigated by Hartree–Fock *ab initio* methods and density functional theory. The electronic spectra have been calculated with the CS INDO S–CI and SDT–CI procedures. The spectral and photophysical behaviour was investigated by stationary and time-resolved techniques. The more stable conformer was found to be the A rotamer in planar or quasi planar form. DFT calculations gave more planar structure than those obtained using HF methodology. The UV–Vis absorption spectrum of 2,3-(PhE)₂F is very similar to that of 3-*cis*- α,ω -diphenylhexatriene. The CS INDO CI analysis of the electronic spectra of all rotamers, with particular attention to the *cis* peak, shows coherence with the presence of A conformer. These very stable compounds show a strong and structured fluorescence indicating that the emitting state is the same as that implied in the absorption process, $|\pi_H\pi_L^-\rangle$ singlet state. These new organic fluorophores may have very interesting applications as fluorescent probes, dye laser medium, scintillators and as π -core for new push–pull polyenes.

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1. Introduction

The characterization of molecular structure and electronic spectrum of a molecule is a central problem in Chemistry and a necessary condition to study its photophysics, photochemistry and (non-linear) optics. For these purposes, several spectroscopic techniques have been developed. In particular, in order to individualize the electronic spectrum, one and two photon absorption spectroscopy, transient spectroscopy and electron-impact spectrometry are used and their results are integrated by theoretical interpretations.

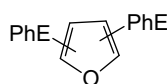
Recently we were able to resolve the problem of rotational isomerism and electronic structure of some conjugated compounds combining UV–Vis absorption spectra, transient spectra and quantum chemistry calculations [1]. Such approach, that is not new, because it starts from the beginning of the molecular quantum mechanics age, has led to some new interesting results. More precisely, we were able to explain the appearance of the “*cis* peak” in the UV–Vis absorption spectrum of some stilbenoid compounds, with *ab initio* HF and DF calculations of their conformers in the electronic ground state and CS INDO CI calculations of

the electronic spectrum [1,2]. As part of our interest on the class of these compounds [1–6], in this paper we extend the previous methodological approach to study the conformations (rotational isomerism), electronic structure, photophysics and other molecular optical properties of di(phenylethenyl) derivatives of furan (Scheme 1) in their *EE* forms.

The introduction of two phenylethenyl (styryl) groups in furan (as well as in thiophene, pyrrole and cyclopentadiene) may lead to different positional isomers, namely the 2,3-, 2,4-, 2,5- and 3,4-di(phenylethenyl) derivatives. The different topologies of these compounds originate conjugated molecular systems with strong differences in the π -electronic structures. For example, in the 2,5-(PhE)₂F (Scheme 2), a spectroscopic behaviour very similar to 3-*cis*- α,ω -diphenyloctatetraene was found [2], whereas in the 2,3-(PhE)₂F (Scheme 3) a 3-*cis*- α,β -diphenylhexatriene-like spectroscopic behaviour is expected, the π -electronic structure of 2,4-(PhE)₂F and 3,4-(PhE)₂F being more complex. The electronic structure of 2,4-(PhE)₂F may be considered deriving from the interaction of a phenylbutadiene moiety and a phenylhexatriene moiety (Scheme 4). Differently, the electronic structure of 3,4-(PhE)₂F is referable to a dimer of interacting phenylbutadienes (Scheme 5). From this qualitative analysis of the *n,n'*-(PhE)₂F electronic structures, it appears suitable to split the four molecules into two groups to be examined separately. The first group includes 2,3-(PhE)₂F and 2,5-(PhE)₂F, the second one 2,4-(PhE)₂F and 3,4-(PhE)₂F.

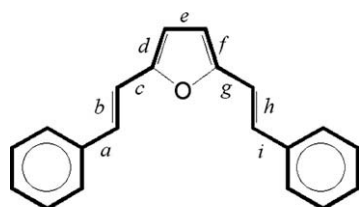
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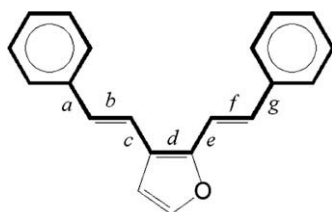
n,n' -(PhE)₂F

Scheme 1.



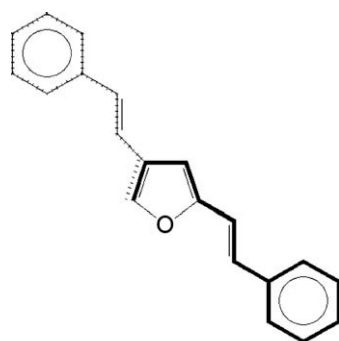
2,5-(PhE)₂F

Scheme 2.



2,3-(PhE)₂F

Scheme 3.



2,4-(PhE)₂F

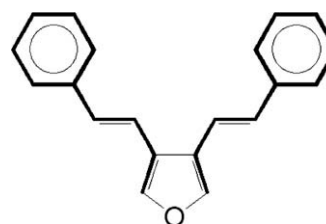
Scheme 4.

In the present work, we have analyzed the rotational isomerism, spectroscopic and photophysical properties of 2,3-(PhE)₂F and 2,5-(PhE)₂F.

2. Computational and experimental procedure

2.1. Computational

A full geometry optimization at HF *ab initio* 6-31G* level and at DFT level using 6-31G* basis set and considering B3-LYP functional was employed to obtain the forms of n,n' -(PhE)₂F conformers. The starting points for the geometry optimization were the planar and non-planar geometries of the rotamers of n,n' -(PhE)₂F. The initial



3,4-(PhE)₂F

Scheme 5.

non-planar geometries were obtained twisting the benzene rings by $\pm\pi/6$ with respect to internal axes starting from planar forms. The HF and DFT optimized geometries were submitted to vibration calculation to investigate whether the convergence points were true energy minima. Some thermodynamical parameters calculated for the gas phase are analyzed. Gaussian 03 computational package [7] was used in all these calculations.

As said in Section 1, the calculations of the singlet excited electronic states and, in consequence, the $S_0 \rightarrow S_n$ absorption spectra, of the “stable” rotamers were performed with the CS INDO CI method that treats valence-shell states only [8]. For recent developments of the CS INDO Hamiltonian, see Ref. [9]. The optimized geometries of the planar conformers of the ground electronic state, as obtained from HF *ab initio* level and DFT calculations, were used in the CS INDO CI calculations of the more stable conformers. For non stable conformers, the optimized non planar form was used.

Details of the CS INDO calculations are not reported, because they coincide with those previously described [10–12]. The configuration interactions were carried out both in the singly-excited scheme (S-CI) and in that involving multiple excitations (SDT-CI). From the discussion on electronic spectra below, it will emerge that the inclusion of the poly-excitations, especially the double ones, is necessary for a correct description of the absorption spectra. For the planar conformations, the MO active space in the CI calculations includes all the MO's antisymmetric with respect to the molecular plane, the π -MO space, while in non planar forms the MO active space is larger.

The frontier orbitals of the molecules, HOMO and LUMO, have been indicated with H and L, respectively. Such notation will be used for the classification of configurations.

2.2. Experimental

The title compounds [13] were synthesized by one of us by Wittig reaction starting from 2-*trans*-(2-phenylethenyl)furan-*n*-carbaldehyde ($n = 3$ or 5) and benzyltriphenylphosphonium bromide

Table 1
Calculated energy difference and BLA among conformers of 2,3-(PhE)₂F

	A planar (non-planar) conformation	B planar (non-planar) conformation	C planar (non-planar) conformation	D planar (non-planar) conformation
ΔE (kJ/mol)				
HF ^a	0 (−0.761, −0.596)	16.093 (6.660)	14.916 (3.929)	41.866 (18.907, 19.650)
DF ^b	0 (0)	12.590 [1–] (8.907)	11.825 [1–] (7.409)	32.585 [2–] (21.323)
BLA (Å)				
HF ^c	0.124	0.127	0.128	0.134
DF ^c	0.082	0.085	0.085	0.090

^a HF *ab initio* calculations at 6-31G* level.

^b DFT calculations with 6-31G* basis set considering B3-LYP functional.

^c BLA = $\frac{1}{2}[\frac{1}{2}(a+g) + c + e - b - d - f]$. Bonds are indicated in Scheme 3. The values are referred to the most stable forms.

Table 2
BLA of conformers of 2,5-(PhE)₂F

	A planar conformation	B planar conformation	C planar conformation
BLA (Å)			
HF ^a	0.113	0.114	0.114
DFT ^a	0.070	0.070	0.070

^a BLA = $\frac{1}{4}[\frac{1}{2}(a+i) + c + e + g - b - d - f - h]$. Bonds are indicated in Scheme 2.

[6]. The *EE* isomers were separated from the reaction mixture by repeated column chromatography on silica gel using petroleum ether as eluent and further purified by preparative HPLC using a Waters apparatus equipped with a Prontosil C30 (20 × 250 mm; 5 μm) column and UV detector. Water/acetonitrile mixtures were used as eluents.

A Perkin–Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The experimental oscillator strength of the principal band (f_p) and that of the *cis* peak (f_c), reported in Tables 3 and 4, was derived by equation 3.49 of Ref. [14] neglecting the refraction index.

The fluorescence spectra were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance less than 0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric measurements. 9,10-diphenylanthracene in de-aerated cyclohexane was used as fluorimetric standard ($\Phi_f = 0.90$ [15]).

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method.

All measurements were performed at room temperature in a 9/1 (v/v) methylcyclohexane/3-methylpentane mixture (MCH/3MP), acetonitrile (ACN), 1/2 (v/v) acetonitrile/water mixture (ACN/H₂O), toluene and benzonitrile (BCN). The fluorescence quantum yields and lifetimes were measured in de-aerated solutions by purging

with nitrogen. The parameters reported in the Tables are averages of at least three independent experiments with mean deviation of ca. 10%.

3. Results and discussion

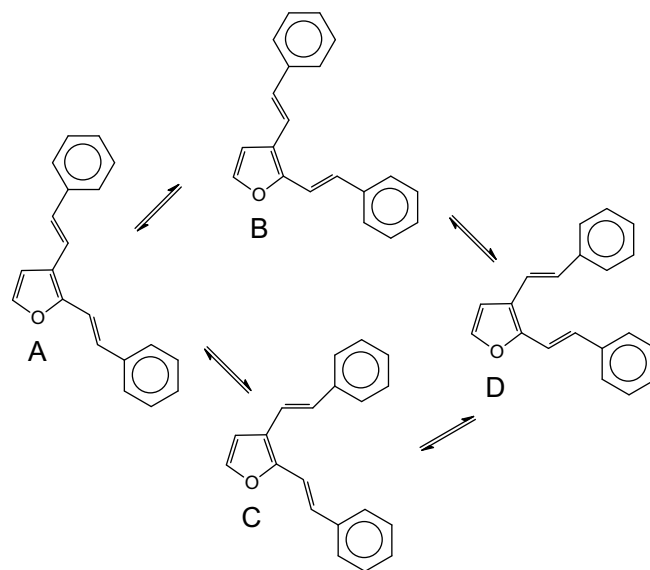
3.1. Conformations and rotational isomerism

3.1.1. 2,3-(PhE)₂F

It is possible to hypothesize the following rotational isomerism (Scheme 6) for the 2,3-(PhE)₂F.

The results of the molecular quantum mechanical calculations on the conformers of Scheme 6 are reported in Table 1, where the total energy is referred to the planar A conformer. Bond length alternation (BLA), related to the difference between the average length of single and double bonds, is also contained in the table. Energetic data analysis indicate that the A conformer is more stable than the other three rotamers, the D conformer being the most destabilized.

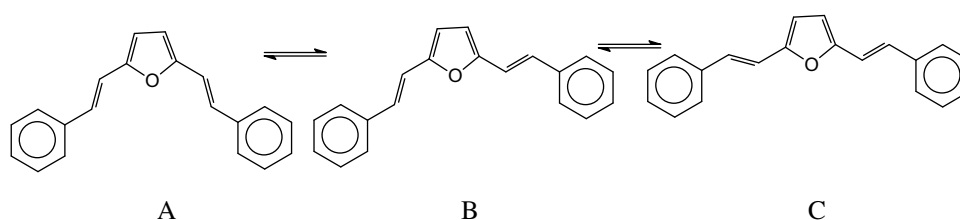
In the HF approximation two non-planar conformations of the A conformer were found slightly more stable of about –0.60 to –0.80 kJ/mol than the planar one. In one of the non-planar conformation the phenyl groups are twisted in phase, in the other they are out of phase. For the other three rotamers (B, C, D), the non-planar conformations are significantly more stable than the planar one, the stabilization energy being about 10–20 kJ/mol. The DFT calculations give more planar conformations; in particular the

**Scheme 6.****Table 3**
CS INDO S-CI and SDT-CI results on $S_0 \rightarrow S_n$ absorption spectra of the A conformer of 2,3-(PhE)₂F

Transition $S_0 \rightarrow S_n$	S-CI			SDT-CI			Exp.	
$1^1A' \rightarrow m^1A'$ ($m = n + 1$)	ΔE (eV)	$f_{(0-n)}$	d (D)	ΔE (eV)	$f_{(0-n)}$	d (D)	ΔE (eV)	$f_{(0-n)}$
$n = 0$	–	–	0.537	–	–	0.724		
1	3.312	1.272	1.895	3.450	0.925	2.125	3.477	0.923 (f_p)
2	4.507	0.560	1.980	4.487	0.555	2.228	4.488	0.554 (f_c)
3	4.690	0.000	2.430	4.496	0.035	1.659		
4	4.704	0.005	1.430	4.679	0.005	1.990		
5	4.998	0.030	2.285	4.948	0.206	2.636		
6	5.149	0.002	0.745	5.066	0.043	5.390		
7	5.442	0.107	3.752	5.483	0.327	1.827	≈5.30	≈0.3
8	5.638	0.456	2.676	5.725	0.143	1.840		
9	6.153	0.055	3.286	5.992	0.229	8.937		

Table 4
CS INDO S-CI and SDT-CI results on $S_0 \rightarrow S_n$ absorption spectra of the A conformer of 2,5-(PhE)₂F

Transition $S_0 \rightarrow S_n$	S-CI			SDT-CI			Exp.	
$1^1A_1 \rightarrow q^1A_1$ ($p = 1, 2, \dots; q = 2, 3, \dots$)	ΔE (eV)	$f_{(0-n)}$	$d(D)$	ΔE (eV)	$f_{(0-n)}$	$d(D)$	ΔE (eV)	$f_{(0-n)}$
$n = 0$	(1^1A_1)	–	–	–	–	1.141		
1	(1^1B_2)	3.097	0.883	2.453	3.306	0.866	3.306	0.861 (f_p)
2	(2^1A_1)	4.377	0.734	3.155	4.512	0.369	4.509	0.367 (f_c)
3		4.693	0.001	2.229	4.875	0.023		
4		4.694	0.007	2.275	4.881	0.002		
5		5.044	0.002	2.090	4.929	0.474		
6		5.067	0.011	0.943	4.984	0.006		
7		5.764	0.063	4.336	5.192	0.292	≈5.28	≈0.30
8		5.789	0.490	0.753	5.522	0.067		
9		6.010	0.172	2.927	5.735	0.011		



Scheme 7.

planar A conformer is the most stable. The phenyl twisting angles of the non planar optimized geometries at HF level are larger than those obtained with the DFT calculations. In particular, phenyl twisting angles found after the optimization procedure are in the range 13–26° for HF and 6–13° for DFT.

Choosing a mean value of 7.0 kJ/mol as energy destabilization for B and C conformers respect to A, and 20.0 kJ/mol for D, the Boltzmann factor indicates a relative presence of about 5% of B and C and a negligible one of D at room temperature. It has to be noted that the relative abundances of the conformers were estimated on the basis of the energy terms neglecting the entropy ones. As a matter of fact, an analysis of the thermodynamic parameters obtained at 298.150 K and 1 atm from the DFT calculations in the gas phase showed that the conformers have a similar entropy.

The vibrational analysis performed on A, B, C and D planar optimized geometries of 2,3-(PhE)₂F indicates the presence of some (from two to four) negative frequencies of very low wavenumber in the HF *ab initio* methodology. In the non-planar optimized geometries these frequencies are all positive, indicating the presence of true energy minima. In the DFT calculations all vibrations are positive in the A planar conformation but there are one or two negative frequencies of very low wavenumbers in the B, C and D planar conformations. The latter disappear in the non-planar optimized geometries. Such results indicate that the B, C and D conformers have non planar geometries in the gas phase.

The data on BLA of Table 1 indicate that the BLA(HF) coincide with those of the standard polyenes, while the BLA(DFT) are significantly smaller. Such findings on BLA are in agreement with the results on conformations discussed above. The larger planarity of DFT optimized geometries respect to the HF ones is connected to a larger estimation of the conjugation in the polyene chain, this aspect being reflected into a less BLA value than classical polyenes.

3.1.2. 2,5-(PhE)₂F

Scheme 7 presents the equilibrium between the *EE* rotamers of 2,5-(PhE)₂F. In Ref. [2] it is shown that the most stable conformer is the A specie. Its conformation is almost planar and shows a significant *cis* peak as found in the UV–Vis absorption spectrum. To complete the conformational analysis of 2,5-(PhE)₂F, the BLA of its conformers obtained at HF and DFT levels is reported in Table 2. Even for this compound, the lower BLA(DFT) indicates a larger conjugation of the polyenic chain.

3.2. UV–Vis absorption spectra

3.2.1. 2,3-(PhE)₂F

Fig. 1 presents the UV–Vis absorption and fluorescence emission spectra of 2,3-(PhE)₂F in MCH/3MP at room temperature. The maximum of the fundamental (principal) absorption band is found at 359 nm; the band is rather strong ($f_p = 0.923$, Table 3) and shows a partial resolved vibrational structure with maxima at 378.5, 359.0 and 341.5 nm, corresponding to “0 ← 0”, “1 ← 0” (maximum) and “2 ← 0” vibronic band.¹ The frequency (wavenumber) of this “progression” is about 1430–1440 cm^{−1} and the inequalities $I_{00} < I_{10}$ and $I_{10} > I_{20}$ on vibronic intensity is verified. On the base of the Franck–Condon principle, we conclude that the electronic excitation causes a significant change of the molecular geometry of 2,3-(PhE)₂F. The second electronic band, of medium intensity ($f_c = 0.554$, Table 3), has two maxima at 273.5 and 282 nm ($\Delta\bar{\nu} = 1100$ cm^{−1}). Further absorption at wavelength less than 250 nm appears.

Comparison of the absorption spectrum of Fig. 1 with that of 3-*cis*- α,ω -diphenylhexatriene of Ref. [16] shows an extraordinary similarity. Because of the perturbation of the furan ring, only a slight red shift of few nm is observed in the spectrum. In particular, there is a strong analogy between the second absorption bands, that display a fine structure with two maxima. The absorption band of 2,3-(PhE)₂F, found at 275 nm, may be named *cis*-peak or *cis*-band as in polyenes and α,ω -diphenylpolyenes [16].

Electronic spectra calculations for the A conformer were made with the planar geometries obtained *via* full optimization at HF and DFT levels. The use of these planar geometries is a consequence of several factors. The principal aspect is that the σ – π coupling in non planar forms of the A conformer is scarce, as consequence of the relatively small twisting angles of phenyl groups. Such aspect has been tested calculating the spectrum of the A conformer of 2,3-(PhE)₂F with planar and non-planar geometries. Very similar results were obtained.

In Table 3 we summarized the CS INDO S-CI and SDT-CI results on the $S_0 \rightarrow S_n$ absorption spectra of the A conformer obtained with DFT planar geometry. The data of the first ten electronic state are reported together with the magnitude (d) of the calculated permanent dipole moment vector ($\mathbf{d}$).

¹ Because of low resolution of the vibrational structure of the electronic bands, the wavelengths and the vibrational classification are approximated.

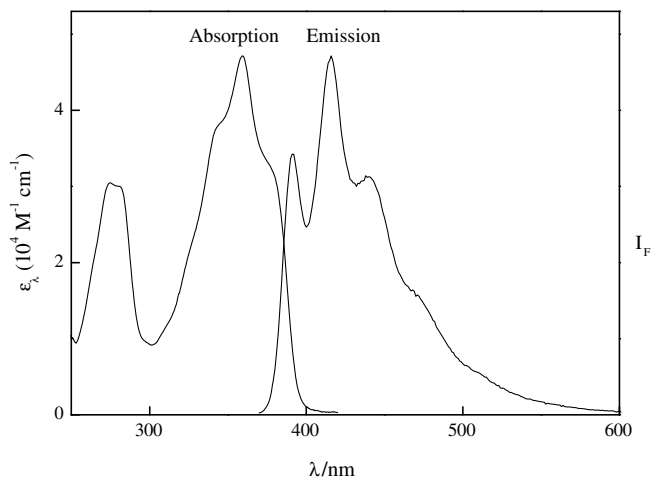


Fig. 1. UV–Vis absorption and fluorescence emission spectra of 2,3-(PhE)₂F in MCH/3MP at room temperature.

The CS-INDO SDT-CI transitions of Table 3 were assigned to the first two bands of the UV–Vis absorption spectrum of 2,3-(PhE)₂F. In the C_s molecular point group, the $\pi \rightarrow \pi^*$ electronic transitions of $1^1A' \rightarrow m^1A'$ type, are allowed and polarized in the molecular plane. Particularly, they are expected to be influenced by the polyene character, and consequently some transitions are polarized along the polyene axis (“molecular long axis”) and other along a “perpendicular” axis (“molecular short axis”). The $S_0 \rightarrow S_1$ ($1^1A' \rightarrow 2^1A'$, $\pi_H \rightarrow \pi_L^*$) transition, long axis polarized, is responsible for the principal band, while the $S_0 \rightarrow S_2$ ($1^1A' \rightarrow 3^1A'$) transition, short axis polarized, is responsible for the *cis* peak. Such polarizations are confirmed by the CS INDO CI results on the direction of the transition moments (a value of 90° was obtained for the angle between the S_1 – S_2 transition moments). Table 3 and SDT-CI wavefunction analysis shows that the polieexcited configurations have an interesting role on the electronic spectrum of this molecule. The S_1 electronic state is characterized by the $|HL\rangle \equiv |\pi_H\pi_L^*\rangle$ singly excited configuration, while the electronic state responsible for the *cis* peak (S_2 state, according to the SDT-CI calculation of Table 3), is characterized by the $|HL+1\rangle$ singly excited and by the $|H^0L^2\rangle$ doubly excited configurations. This behaviour is similar to that found in the electronic states of other stilbenoid compounds recently investigated [1,2].

The comparison of the CS INDO CI results for the non-planar B, C and D conformers with the absorption spectrum of Fig. 1, shows an oscillator strength of the *cis* peak much higher than that of the $S_0 \rightarrow S_1$ transition. This fact, in disagreement with the experimental finding, excluded a significative presence of the B, C and D rotamers at room temperature.

Data in Table 3 show that the permanent dipole moment increases in passing from the S_0 ground state to the S_n excited states, indicating an increase of the charge transfer character. Therefore, a detectable solvent effect on the absorption and emission spectrum may be expected (see below).

3.2.2. 2,5-(PhE)₂F

The UV–Vis absorption and fluorescence emission spectra of 2,5-(PhE)₂F in MCH/3MP at room temperature are shown in Fig. 2. In Table 4, we summarized the CS INDO S-CI and SDT-CI results on the $S_0 \rightarrow S_n$ absorption spectra of the A conformer obtained with DFT planar geometry, having the C_{2v} molecular point group. Only the lowest transitions were reported in Table 4 together with the calculated dipole moments. From symmetry analysis, the vector **d** is directed along the C_{2v} symmetry axes. The discussion developed in Ref. [2] showed that the principal absorption band

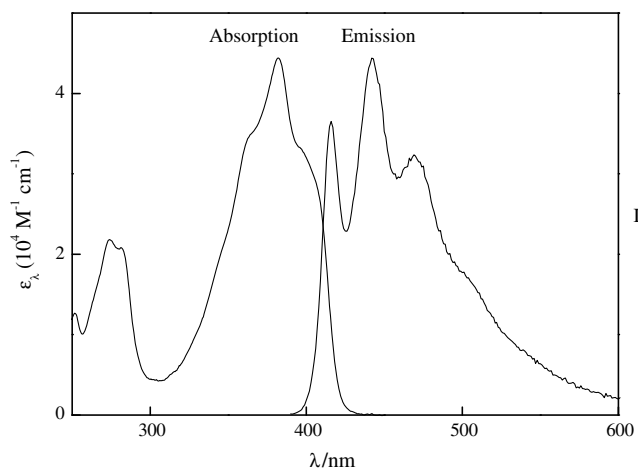


Fig. 2. UV–Vis absorption and fluorescence emission spectra of 2,5-(PhE)₂F in MCH/3MP at room temperature.

of Fig. 2 with maximum at 382 nm is the $S_0 \rightarrow S_1$ ($1^1A_1 \rightarrow 1^1B_2$, $\pi_H \rightarrow \pi_L^*$) transition long axis polarized, and the *cis* peak around 275 nm (maxima at 274 and 282 nm, $\Delta\bar{\nu} = 1040 \text{ cm}^{-1}$) is the $S_0 \rightarrow S_2$ ($1^1A_1 \rightarrow 2^1A_1$) short axis polarized transition. The vibrational analysis of the principal absorption band indicates that the vibronic maxima are found at 404.0, 382.0 and 362.0 nm, corresponding to the “0 ← 0”, “1 ← 0” (maximum) and “2 ← 0” vibronic band. The wavenumber of this progression is about $1430\text{--}1440 \text{ cm}^{-1}$. In the principal band of this spectrum the inequality $I_{00} < I_{10}$ and $I_{10} > I_{20}$ in the vibronic intensity is verified, pointing out that the electronic excitation causes a significant change of the molecular geometry also in the case of 2,5-(PhE)₂F.

In general, Table 4 shows that the permanent dipole moment of the S_n excited states is greater than that of the S_0 ground state, indicating an increase of the charge transfer character also for this compound.

Note that the red shifts of the principal absorption band of 2,5-(PhE)₂F with respect to that of 2,3-(PhE)₂F is 23 nm, while in the corresponding α,ω -diphenylpolyenes it is 20 nm.

3.3. Fluorescence emission spectra and photophysics

The fluorescence emission spectra of 2,3-(PhE)₂F and 2,5-(PhE)₂F and their comparison with the absorption spectra (Figs. 1 and 2) show interesting behaviours. The emission spectra display a well resolved vibrational structure, better of that observed in the principal absorption band. As a general rule, such spectral behaviour is connected to a larger planarity and rigidity of the geometry of the emitting state with respect to the S_0 ground state. The emission vibronic band maxima were at 392, 415 and 441 nm, corresponding to “0 → 0”, “0 → 1” (maximum) and “0 → 2” vibronic band, for 2,3-(PhE)₂F and at 416, 442 and 470 nm, respective “0 → 0”, “0 → 1” (maximum) and “0 → 2” vibronic band, for 2,5-(PhE)₂F. The approximate wavenumber of these progressions is about $1400\text{--}1420 \text{ cm}^{-1}$. For both molecules, Figs. 1 and 2 illustrate that the fluorescence emission spectrum is approximately a mirror image of the absorption spectrum.

The fluorescence spectrum does not depend on λ_{exc} and the excitation spectrum well overlaps the absorption spectrum for both the compounds. These evidences, together with the observed monoexponential fluorescence decays, point to the presence of a prevalent emissive species, in agreement with the theoretical calculations.

Table 5 contains the measured photophysical data and the Stokes-shift ($\Delta\bar{\nu}_S = \bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{em}}$) calculated from the spectra of Figs. 1 and 2. $\Delta\bar{\nu}_{00}$ corresponds to the 0–0 vibronic bands and $\Delta\bar{\nu}_{\text{max}}$ to the maxima of the spectra. The mean values are 810 cm^{-1} for $\Delta\bar{\nu}_{00}$ and 3660 cm^{-1} for $\Delta\bar{\nu}_{\text{max}}$. The small values of the Stokes-shift clearly show that both bands are associated with the same excited state. On the contrary, larger values were observed for diphenylhexatriene (DPH) and diphenyloctatetraene (DPO) [17,18]. It has

Table 5
Photophysical data of 2,3-(PhE)₂F and 2,5-(PhE)₂F in MCH/3MP

Molecule	Stokes-shift $\Delta\bar{\nu}_S$ (cm ⁻¹)	Quantum yield Φ_f	Lifetimes τ_f, τ_r, τ_0 (ns)	k_f (10 ⁸ s ⁻¹)
2,3-(PhE) ₂ F	$\Delta\bar{\nu}_{00} = 910$ $\Delta\bar{\nu}_{\text{max}} = 3760$	0.75	$\tau_f = 3.0$ $\tau_r = 4.0$ $\tau_0 = 2.02^a$ (3.7–1.8) ^b	2.5
2,5-(PhE) ₂ F	$\Delta\bar{\nu}_{00} = 714$ $\Delta\bar{\nu}_{\text{max}} = 3554$	0.65	$\tau_f = 4.3$ $\tau_r = 6.8$ $\tau_0 = 3.59^a$ (4.5–2.3) ^b	1.5

^a ($\tau_0 = 0.682 \times \bar{\nu}_0^2 \times f$) [20].

^b $\frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \int \frac{(2\bar{\nu}_0 - \bar{\nu})}{\bar{\nu}} \varepsilon(\bar{\nu}) d\bar{\nu}$ [14] $n = 1.00, \dots$

Table 6Spectral, photophysical and photochemical parameters for 2,3-(PhE)₂F in different solvents at room temperature

Solvent	α (ϵ) ^a	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{flu}}$	$\Delta\tilde{\nu}_{00}$ (cm ⁻¹)	Φ_F	τ_F (ns)	k_F (10 ⁸ s ⁻¹)	$\Phi_{EE \rightarrow ZE}$	$\Phi_{EE \rightarrow EZ}$
MCH/3MP	0.251 (2.01)	359	415	810	0.75	3.0	2.5	0.007	0.003
ACN	0.212 (35.9)	358	418	1400	0.26	1.5	1.7	0.088	0.038
ACN/H ₂ O	0.208 (65.4)	359	420	1530	0.16	1.0	1.6		
Toluene	0.292 (2.38)	364	422	850	0.68	2.2	3.1		
BCN	0.308 (25.2)	367	428	1020	0.43	1.5	2.9		

^a From Ref. [19]; the solvent polarizability (α) was calculated by the refractive index [$\alpha = (n^2 - 1)/(n^2 + 2)$].

to be noted that the Stokes-shift of Ref. [18] is calculated by the formula $\Delta\tilde{\nu}_S = \frac{1}{2}(\tilde{\nu}_{\text{abs av}} - \tilde{\nu}_{\text{em av}})$.

The fluorescence quantum yields are greater than 0.6, indicating that the radiative decay is the main deactivation channel for these compounds. The observed fluorescence lifetime is 3.0 ns for 2,3-(PhE)₂F and 4.3 ns for 2,5-(PhE)₂F in MCH/3MP at room temperature. Table 5 contains also the calculated radiative lifetime obtained by the absorption spectra (τ_0) and by the photophysical data ($\tau_r = \tau_f/\Phi_f$). These radiative lifetimes are similar. Again we have indication that emission and absorption involve the same excited electronic state.

The results of the solvent effect on the spectral behaviour and the photophysical and photochemical parameters are collected in Tables 6 and 7 and Figs. 3 and 4. The increase of the polarity of the solvent (on passing from MCH/3MP to ACN and ACN/H₂O) did not affect the absorption spectrum but caused a red shift of the emission that leads to an increased Stokes shift ($\Delta\tilde{\nu}_{00}$). This fact is obviously due to a larger stabilization of the singlet excited state by the polar solvent. An important reduction of the fluorescence quantum yield was also observed in these solvents, accompanied by an increase of the photoisomerization that points to a reduction of a sizable energy barrier for the rotation around the two double bonds. As a matter of fact the two distyrylfurans practically do not react in non-polar solvent ($\Phi < 0.01$) while an increase higher than one order of magnitude for the photoisomerization quantum yield was observed in ACN. In the case of the asymmetric compound (2,3-(PhE)₂F), two photoproducts with different quantum yields (see Table 6) were found, assigned to the geometrical isomers (EZ and ZE) where one or the other double bond isomerized. Both these photoproducts reconverted to EE by irradiation. By comparing the reactivity of the two compounds it could be argued that the presence of oxygen in ortho position with respect to the double bond inhibits the rotation. If this is the case, the larger value of the photoisomerization quantum yield could be assigned to the rotation of the double bond attached at the 3 position of the furan ring.

The increase of the solvent polarizability (on going from MCH/3MP to toluene and BCN) produced a net red shift of both the absorption and emission spectra leaving the Stokes shifts practically unchanged.

Looking at Tables 6 and 7 it is evident that the component of the induced dipole moment is important in determining the energy of the transition in agreement with the calculations that predicted a more polar excited singlet state.

Table 7Spectral, photophysical and photochemical parameters for 2,5-(PhE)₂F in different solvents at room temperature

Solvent	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{max}}^{\text{flu}}$	$\Delta\tilde{\nu}_{00}$ (cm ⁻¹)	Φ_F	τ_F (ns)	k_F (10 ⁸ s ⁻¹)	$\Phi_{EE \rightarrow ZE}$
MCH/3MP	382	442	710	0.65	4.3	1.5	0.0003
ACN	381	446	1370	0.46	3.6	1.3	0.048
ACN/H ₂ O	382	448	1480	0.34	2.4	1.4	
Toluene	387	451	750	0.68	2.9	2.3	
BCN	390	458	890	0.46	2.1	2.2	

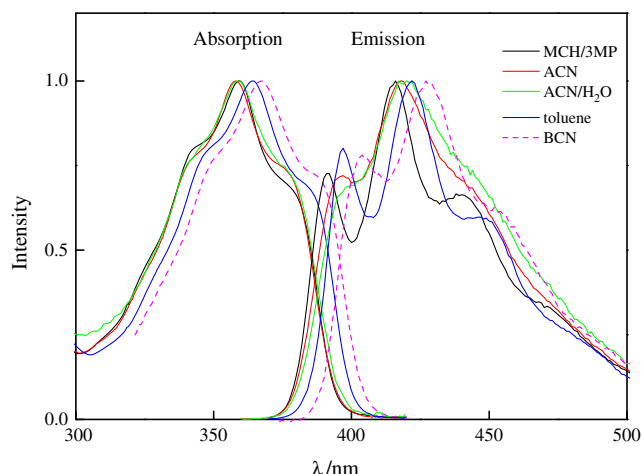


Fig. 3. UV-Vis absorption and fluorescence emission spectra of 2,3-(PhE)₂F in different solvents at room temperature. This figure can be viewed in colour in the online version of the paper (doi:10.1016/j.chemphys.2008.08.005).

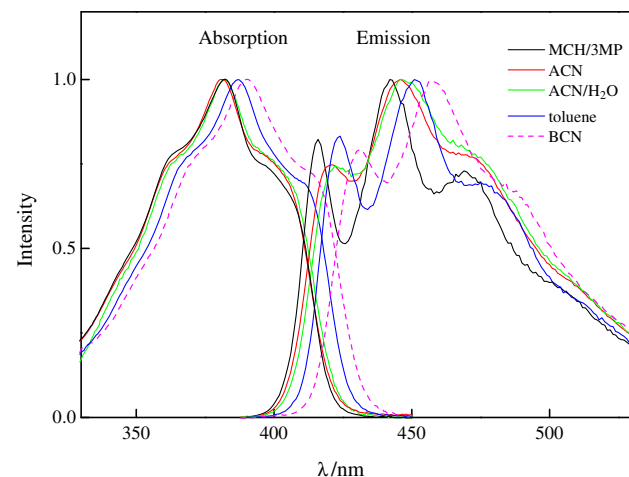


Fig. 4. UV-Vis absorption and fluorescence emission spectra of 2,5-(PhE)₂F in different solvents at room temperature. This figure can be viewed in colour in the online version of the paper (doi:10.1016/j.chemphys.2008.08.005).

The derived kinetic parameter of fluorescence is high (of the order of 10⁸ s⁻¹) and practically the same (within the experimental error) for both compounds in the different solvents in agreement with the theoretical finding of a same state involved in the absorption and emission processes.

Moreover, a comparison of the fluorescence emission spectra and photophysical data of the present compounds (Figs. 1 and 2 and Table 5) with those of all-*trans* α,ω -diphenylpolyenes, in particular DPH and DPO [17,18,20,21], is interesting. The characteristics of the emission and photophysical behaviour of all-*trans* α,ω -diphenylpolyenes have been widely studied in the last 40 years. It is well known that the most usual interpretation of their

photophysics and spectroscopy, is based on the role played by the two lowest excited states, the forbidden 2^1A_g state and the allowed 1^1B_u state [21]. Either in all-*trans* DPH or all-*trans* DPO, the first singlet excited state S_1 is the 2^1A_g forbidden one, followed by the allowed 1^1B_u state S_2 , the main emission being due to the symmetry forbidden $2^1A_g \rightarrow 1^1A_g$ transition, caused by vibronic coupling between the two excited electronic states [22]. On the contrary, in the present cases, the emission and photophysics are consistent with the involvement of the allowed state, i.e. the emission is due to the $2^1A' \rightarrow 1^1A'(\pi_L^* \rightarrow \pi_H)$ transition of the prevalent A rotamer in the planar form.

4. Conclusions

The main results of this study concern the rotational isomerism, electronic structure, fluorescence emission spectra and photophysics of 2,3- and 2,5-di-(phenylethenyl)furan. A combined theoretical and experimental approach led to the following conclusions:

- The more stable conformer of the studied compounds is the planar or quasi-planar A (*trans-trans*) rotamer. The conformer of 2,3-(PhE)₂F reminds the usual conformation of 3-*cis*- α,ω -diphenylhexatriene.
- DFT calculations on conformations give smaller BLA and more planar structure than those obtained using the HF methodology. A more conjugated π -chain is thus obtained.
- The UV–Vis absorption spectrum of 2,3-(PhE)₂F is very similar to that of 3-*cis*- α,ω -diphenylhexatriene. The CS INDO CI analysis of the *cis* peak indicates coherence with the presence of the A conformer.
- The fluorescence emission spectra and photophysics show that the emitting state is the same as the absorbing one ($|\pi_H\pi_L^*\rangle$ singlet state). It is related to the 1^1B_u state of all-*trans* polyenes. No inversion between the allowed and “forbidden” state is observed or calculated contrary to the case of all-*trans* DPH and DPO.
- The results of the spectroscopic and photophysical study suggest that these two new organic fluorophores may have very interesting applications as fluorescent probes, dye laser medium, scintillators and as π -core for new push–pull polyenes.

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