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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.

## 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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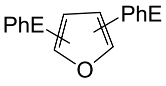
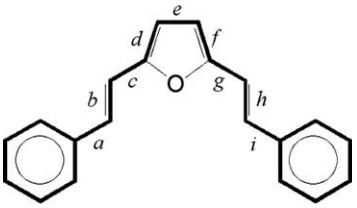


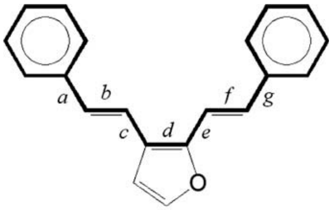
*n,n'*-(PhE)$_2$F

**Scheme 1.**



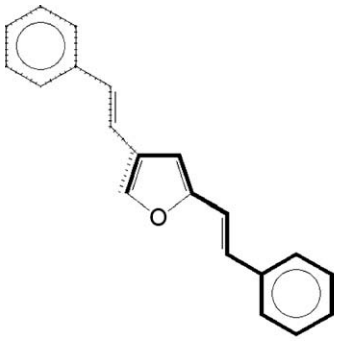
2,5-(PhE)$_2$F

**Scheme 2.**



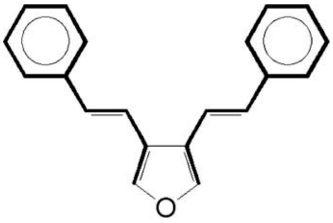
2,3-(PhE)$_2$F

**Scheme 3.**



2,4-(PhE)$_2$F

**Scheme 4.**



3,4-(PhE)$_2$F

**Scheme 5.**

In the present work, we have analyzed the rotational isomerism, spectroscopic and photophysical properties of 2,3-(PhE)$_2$F and 2,5-(PhE)$_2$F.

## 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)$_2$F conformers. The starting points for the geometry optimization were the planar and non-planar geometries of the rotamers of *n,n'*-(PhE)$_2$F. The initial 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)$_2$F

| | 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 | 16.093 | 14.916 | 41.866 |
| | (−0.761, −0.596) | (6.660) | (3.929) | (18.907, 19.650) |
| DF[b] | 0 | 12.590 [1−] | 11.825 [1−] | 32.585 [2−] |
| | (0) | (8.907) | (7.409) | (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] $\mathrm{BLA} = \frac{1}{3}[\frac{1}{2}(a+g)+c+e-b-d-f]$. Bonds are indicated in Scheme 3. The values are referred to the most stable forms.