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PHOTOPHYSICAL PROPERTIES OF PERYLENE MOLECULE

LARISA MILENA ŢIMBOLMAŞ[1], V. CHIŞ[1*]

ABSTRACT. In this work we investigated computationally the photophysics of the perylene molecule using the time-dependent Density Functional Theory (TD-DFT). Particularly, we were interested in the vertical emission energy and radiative fluorescence lifetime of the investigated molecule. Using adequate models and proper computational methodologies we were able to satisfactorily predict the experimentally reported photophysical properties of the perylene core.

Keywords: *perylene; photophysics; excited state; TD-DFT; radiative lifetime*

1. INTRODUCTION

Perylene derivatives, consisting of a perylene core functionalized with different substituents, attached at their terminal and/or bay-positions [1], have been used for many years as technical pigments due to their high temperature, photo and chemical stabilities [2]. Besides, in the last years, such compounds

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[1] *Babeş-Bolyai University, Faculty of Physics, 1 Kogălniceanu, RO-400084 Cluj-Napoca, Romania*
[*] *Corresponding author: vasile.chis@phys.ubbcluj.ro*

gained a great popularity because of their use in optical devices [3-5]. These π conjugated dyes show high photosensitivity and high electron mobility (the charge-carrier mobilities are between 1 $cm^2v^{-1}s^{-1}$ and 10 $cm^2v^{-1}s^{-1}$) [3]. Also, their photophysical properties, particularly the sensitivity of their fluorescence lifetime to the pH, render them very useful as probes for live cell fluorescence lifetime imaging [6].

The photophysical properties of such derivatives are expected to be similar to those of the perylene core. However, in spite of numerous works reported on the absorption and emission properties of perylene derivatives, surprisingly few studies deal with its photophysical properties [3, 7-13].

Besides being a distinct parameter of the molecular excited states, independent of concentration, the fluorescence lifetimes are fundamental parameters for the fluorescence lifetime imaging microscopy (FLIM). They show unique properties which render them very useful for getting information related to the changes of the molecular environment, micro-viscosity, pH, identification of the components in a mixture, or for inter-molecular interactions [14]. Therefore, the accurate determinations of these parameters by experimental or computational techniques are highly needed [15].

While the fluorescence lifetime can be measured nowadays with great accuracy by using the Time-Correlated Single Photon Counting (TCSPC) technique [16], however, its estimation by quantum chemical calculations imposes challenges due to the fact that it requires the optimization of the excited state geometries and the calculation of the dipole moment strength corresponding to the energetic minimum of the excited state. This is why a reduced numbers of studies were reported till now, having as subject the quantum chemical calculation of this parameter [17, 18].

In this study we were interested to obtain computationally the excitation and emission energies and the radiative fluorescence lifetime of the perylene molecule. An interesting and useful characteristic of the molecule is represented by its upconverting properties in sensitized systems [11]. In addition, due to its relatively small size and high symmetry (D_{2h}), the perylene core is an excellent model for testing different calculation methodologies adapted to various molecular properties. Of particular importance are the absorption and emission energies, as well as the radiative lifetime.

Using the model of vertical transition, the radiative emission rate can be written as [19]:

$$k_r = \frac{1}{\tau_r} = \frac{4}{3}\frac{\Delta E^3}{c^3}\mu_{10}^2 \quad (1)$$

where c is the speed of light, ΔE is the energy of transition S1 → S0 and μ_{10}^2 is the transition dipole strength. ΔE and μ_{10} must be evaluated for the energy minimum corresponding to the excited state of the molecule, including solvent effects [17]. The fluorescence lifetime is very sensitive to the conformation of the molecule and to the environment, so any change in the surroundings of the molecule leads to important changes of this parameter [40].

The fluorescence lifetime, defined as the time after which the fluorescence signal intensity (the number of molecules remaining in the excited state) decreases to 1/e of its initial value, can be write using the radiative and non-radiative rates as:

$$\tau_f = 1 / (k_r + k_{nr}) \quad (2)$$

The rate of radiative de-excitation corresponds to the radiative lifetime k_r, and the non-radiative de-excitation rate corresponds to the non-radiative lifetime:

$$\tau_r = 1/ k_r \text{ and } \tau_{nr} = 1/k_{nr} \quad (3)$$

The fluorescence total lifetime τ_f can be written in terms of τ_r şi τ_{nr} as:

$$\tau_f = \frac{\tau_r \tau_{nr}}{\tau_r + \tau_{nr}} \quad (4)$$

The fluorescence emission efficiency (quantum yield) of a fluorophore is defined as the ratio of the number of photons emitted and the number of photons absorbed by the sample or, in other words, the fraction of molecules returning from the excited state S1 to the ground state S0 by radiative emission [20]. This parameter can be estimated based on the two radiative and non-radiative rate constants [21]:

$$\Phi_f = \frac{k_r}{k_r+k_{nr}} = \frac{\tau_f}{\tau_r} \tag{5}$$

Alternatively, τ_f can be obtained from the recorded absorption and emission spectra of the fluorophore, based on the Strickler-Berg equation [7]:

$$\frac{1}{\tau_f} = 2.88 \cdot 10^9\, n^2 \ < \tilde{\upsilon}_0^{-3} >^{-1} \ \frac{g_f}{g_e} \int \epsilon(\upsilon)\, d\ln(\nu) \tag{6}$$

where integration is done over the entire fluorophore absorption band. Here, n is the refractive index of the solvent, $\widetilde{\upsilon_0}$ is the wave number corresponding to the absorption maximum, ε is the molar extinction coefficient and g_f and g_e are the degenerations of the fundamental and excited state, respectively.

2. COMPUTATIONAL DETAILS

The DFT and TD-DFT calculations were performed using the Gaussian 09 Rev. E.01 [22]. For both, DFT and TD-DFT methodology we used the B3LYP [23-26], M06-2X [27] and APFD [28] exchange correlation functionals with Pople style basis sets [29, 30]. The geometries of fundamental and excited states were optimized, and the type of minima obtained was confirmed by the frequencies calculation on each optimized geometry, performed at the same level of theory as that used for geometry optimization. Absorption and emission spectra were calculated using the TD-DFT [31] methodology implemented in the Gaussian 09 program. Figures representing the structures of Perylene have been created using the Mercury 3.9 program [32]. Solvent effects have been accounted for by using the Polarizable Continuum Model (PCM) [33] and the Universal Solvation Model Based on Solute Electron Density (SMD) [34].

3. RESULTS AND DISCUSSIONS

Experimental absorption and emission spectra of perylene in cyclohexane were constructed based on data from ref. [35] and they are presented in Fig. 1. As observed, the absorption spectrum [35] is dominated by the vibronic structure of the first π-π* S0 -> S1 electronic transition with the 0-0 peak at 436 nm. The energy difference between the first two peaks in the absorption spectrum corresponds to a vibration with 1574 cm^{-1} wavenumber. A normal mode at 1567 cm^{-1} wavenumber was calculated for S1 state of perylene in cyclohexane at SMD-B3LYP/6-311++G(2d,p) level of theory, and it corresponds to the C=C stretching vibration along the longitudinal axis of the molecule. This is similar to the case of perylene bis-imide reported previously by our group [36].

As shown in Table 1, the available experimental photophysical data for perylene are quite dispersed, particularly in terms of its fluorescence lifetime. The molecule was studied experimentally in the gaseous phase [9] but also in dilute cyclohexane [10], toluene [3,11], acetone [12] or methanol [13] solutions. The reported 0-0 transition wavelengths are 437.5 nm in cyclohexane [10] and 438.6 nm in toluene. Dalavi et al. [12] reported λ_{max} = 434 nm in acetone and Torres et al. [3] reported for perylene in toluene at room temperature λ_{max} for absorption at 440 nm and λ_{max} for emission at 444 nm. Thus, a minor influence of the solvent on the absorption and emission energies was observed. Contrary, large differences were noted for the measured lifetimes by different groups.

Thus, the reported experimental values of the fluorescence lifetime (τ_f) of perylene are: 6.40 ns in cyclohexane [10], 4.21 ns in toluene [3], 3.78 ns in toluene [11] and 3.63 ns in methanol [13].

Based on the Strickler-Berg equation [7] and using the absorption and emission spectra taken from ref. [38] we obtained a value of 4.66 ns in cyclohexane.

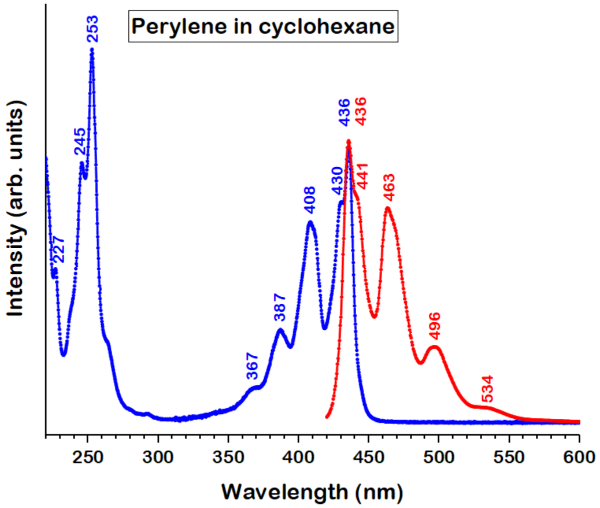

Fig. 1. Absorption and fluorescence spectra of perylene in cyclohexane (adapted from ref. [35]).

Table 1. Available experimental photophysical parameters of perylene

Reference	**[9]**	**[7]**	**[37]**	**[10]**	**[35, 38]**	**[11]**	**[3]**	**[13]**	**[12]**
Solvent	Gas-phase	Cyclo-hexane	Cyclo-hexane	Cyclo-hexane	Cyclo-hexane	Toluene	Toluene	Ethanol	Acetone
$\lambda_{max}^{abs}(nm)$	415.4	n.a.	436	437.5	436	438.6	440	n.a.	434
$\lambda_{max}^{ems}(nm)$	n.a.	n.a.	n.a.	n.a.	436	n.a.	444	n.a.	n.a.
τ_f(ns)	3.88-4.16	4.79	4.70	6.40	4.66***	3.78	3.80	3.63	n.a.
Φ	0.97	0.89	n.a.	0.93	0.94	0.89	0.95	n.a.	n.a.
τ_r (ns)*	4.00-4.29	5.38	n.a.	6.88	4.96	4.26	4.00	n.a.	n.a.
τ_{nr}(ns)**	129.33-137.28	43.68	n.a.	91.73	77.04	34.36	76.00	n.a.	n.a.

* calculated based on eq. (5)

** calculated based on eq. (4)

*** calculated based on eq. (6)

na – not available

We mention that the theoretical data presented in this study correspond to the perylene in cyclohexane and the position of the absorption and emission bands were obtained without considering the vibronic structure of the two spectra.

Computational data provided by using three functionals APFD, B3LYP and M06-2X are presented in Table 2. Excitation and emission energies (in nm) correspond to the vertical transitions. The calculated transitions dipole strength calculated on the minimum structure of the excited state of perylene were also included in Table 2.

To compute the vertical emission energy, which is the difference between the excited state energy calculated on the optimized geometry and the ground state energy calculated on the excited state geometry, it is necessary to optimize both the ground and excited state of the investigated molecule. The estimation of the 0-0 transitions also requires a frequency calculation for the excited state.

Table 2. Calculated photophysical parameters of perylene in cyclohexane

Functional	**Basis set**	**Solvation model**	$\lambda_{max}^{ex\ vert}$ **(nm)**	$\lambda_{max}^{ems\ vert}$ **(nm)**	**Dipole strength (a.u.)**	**τ_r (ns)**
APFD	6-311+G(2d,p)	SMD	453.8	523.0	8.0710	8.75
B3LYP	6-31+G(2d,2p)	PCM	462.3	528.3	7.7158	9.43
B3LYP	6-31+G(d,p)	CPCM	462.5	526.2	8.2569	8.71
M06-2X	6-31+G(d,p)	CPCM	402.4	480.0	8.7928	6.21
M06-2X	6-31+G(d,p)	PCM*	401.0	458.0	8.4905	5.59
M06-2X	6-311G(d,p)	CPCM	393.9	472.4	8.6656	6.01
M06-2X	6-31G(d)	CPCM	385.7	458.0	8.6445	5.48

ex – excitation; vert – vertical; ems – emission; * - state specific solvation

As observed in Table 2, the B3LYP functional provides higher absorption λ_{max} than the experimental values, this behavior of the B3LYP functional being well-known in the literature [39]. However, for the emission energies, the discrepancy between experiment and theory is much worse, with an unacceptable difference of cca. 90 nm. Obviously, this behavior affects drastically the calculated radiative fluorescence lifetime which is significantly higher than the experimental one.

APFD functional, even though coupled to a very flexible triple-zeta basis set, brings some improvement on the calculated excitation energy but still provides unsatisfactory results for the emission energy and the radiative lifetime.

Contrary to B3LYP and APFD, the M06 xc functional systematically provides higher excitation and emission energies compared to B3LYP and APFD. While λ^{ex} are more than 35 nm larger than the experimental value, the vertical emission wavelengths are in qualitative agreement with the experimental counterpart. As seen in Table 2, in case of M06-2X/6-31G(d) and state-specific solvation-M06-2X/6-31+G(d,p) levels of theory, the agreement with experiment is quantitative. This situation is reflected in the calculated radiative lifetimes, which are significantly lower, and closer to the experimental value.

One should remark also the effect of the diffuse functions mixed in the basis set; it seems that such functions decrease the vertical emission energy and decrease the radiative lifetime.

Fig.4 shows the calculated bond lengths for perylene in its ground and excited state. Because of the high symmetry of

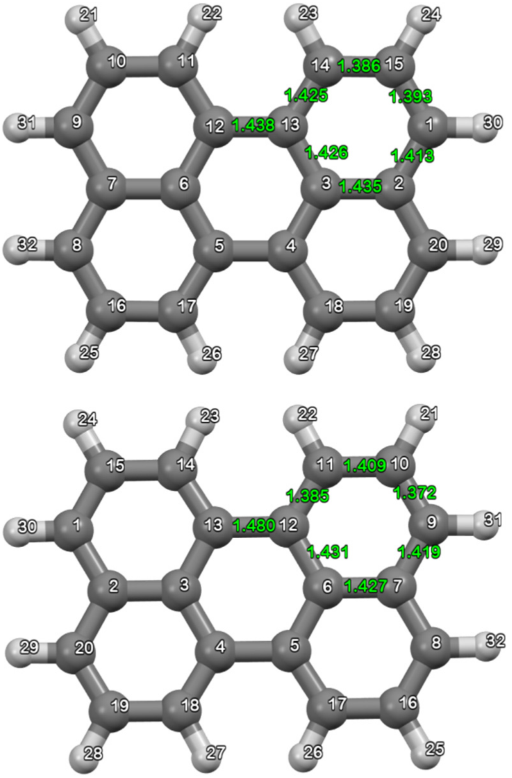

Fig. 4. Bond lengths for the ground state (bottom) and excited state (top) of the perylene molecule in cyclohexane, calculated at M06-2X/6-31+G(d,p) level of theory.

the molecule, only the non-redundant bond lengths are displayed. First of all, it is observed that the molecule retains its planarity when passing from the ground state to the excited state. It is also noticed that the molecule contracts the C12-C13, C4-C5 and C14-C15 bond lengths as a result of electronic excitation. A contrary variation is seen in the case of bonds that are not parallel to the long axis of the molecule. The lengths of CH bonds as well as the valence angles do not change appreciably as a result of transition between the two states.

Similar geometric distortions have been noted for the perylene bis-imide derivative [36].

4. CONCLUSIONS

The purpose of this study was to describe the parameters of excited states for the perylene molecule.

It was shown that the APFD and B3LYP functionals provide vertical excitation energies in agreement with the experiment, but much too higher vertical emission energies. Conversely, the M06-2X functional performs bad for reproducing the excitation energies but it provides much better values for the vertical emission energies.

Inclusion of the diffuse functions into the basis set leads to a drastic decrease of the emission energy and consequently an increase of the calculated radiative fluorescence lifetime for perylene.

For obtaining reliable DFT calculated radiative lifetimes for perylene (and perylene derivatives) we recommend the use of M06-2X functional, coupled to the 6-31+G(d,p) basis set. It is also concluded that state-specific solvation of the excited state is mandatory for reaching quantitative agreement between the calculated and experimental photophysical parameters.

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