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Calculation of the absorption wavelength of dyes using time-dependent density-functional theory (TD-DFT)

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Abstract

The absorption wavelengths and oscillator strengths of a series of organic dyes important for the dye industry (indigo, azobenzene, phenylamine, hydrazone, anthraquinone, naphthoquinone and cationic dyes) were calculated using time-dependent density-functional theory. The results were compared with experimental data. TD-DFT correctly reproduced the visible absorption of the dyes.

Keywords: Organic dyes; TDDFT; Absorption wavelength; Oscillator strength

1. Introduction

Dyes and pigments are key materials in many applications such as thermal transfer or ink jet printers, CD-R, DVD and OPC, both as the source of color and as providers of other properties such as diffractive index or conductivity. The design of functional dyes of specific color and discrete character is essential for the development of contemporary devices.

Quantum chemistry can be a powerful tool in the design of dyes and has already played an important role. The Pariser–Parr–Pople method (PPP) [1,2] was used originally and is still employed to predict the absorption characteristics of dyes. However, this method is restricted to conjugated planar molecules and semi-empirical CNDO/S [3] as well as INDO/S [4] methods have been proposed [5] and variously used [6,7].

Further accuracy, beyond that achieved using semi-empirical methods, is needed for the design of new dyes. Recently, time-dependent density-functional theory (TD-DFT) for the calculation of excitation energies and oscillator strengths of molecules has been implemented in several quantum chemistry packages [8–12]. This method combines the advantages of density functional theory and time-dependent formalism allowing the accurate determination of excited state properties [13–16]. The technique can deal with the same accuracy for both medium and large molecules. However, only a few reports of the use on the TD-DFT method for the calculation of the excited states of large organic molecules have been published [17,18].

In this paper, we present a systematic study, using TD-DFT calculations, of the maximum absorption wavelengths of a series of typical organic dyes important for the dye industry. The calculated results are compared with available experimental data. We have previously accomplished

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a similar study using the semi-empirical INDO/S method [5]. Our purposes in the present work are: (i) to determine the most appropriate basis set and functional; (ii) to determine the accuracy with which TD-DFT can predict the absorption wavelength of organic dyes; (iii) to determine the ability of TD-DFT to reproduce spectral shifts observed within a family of dyes.

2. Computational methods

TD-DFT generalizes density-functional theory to a time-dependent situation wherein a system is subject to a time-dependent perturbation which modifies its external potential. Within Kohn–Sham formalism, time-dependent Kohn–Sham equations can be derived by assuming the existence of an effective potential for an independent particle model whose orbitals give the same density as that of the interacting system. Within response theory, transition energies and oscillator strengths can be determined from the response of the charge density to a perturbation (for a review concerning TD-DFT in molecular applications, see [13]).

TD-DFT is particularly well suited to low-energy valence excited states which can be described by combinations of single excitations but should also work well for large, conjugated molecules. The main drawback of TD-DFT, inherent to any DFT approach, is the choice of the exchange-correlation functional.

We have selected the following important dyes from those used in industry: indigo, azobenzene, phenylamine, hydrazone, anthraquinone, naphthoquinone and cationic dyes. For each family of dyes, three to five different structures were used (Fig. 1). The structure of each dye was optimized using the DFT method and B3LYP functional [19].

In order to determine the most appropriate functional and basis set, the TD-DFT absorption wavelengths and oscillator strengths of several

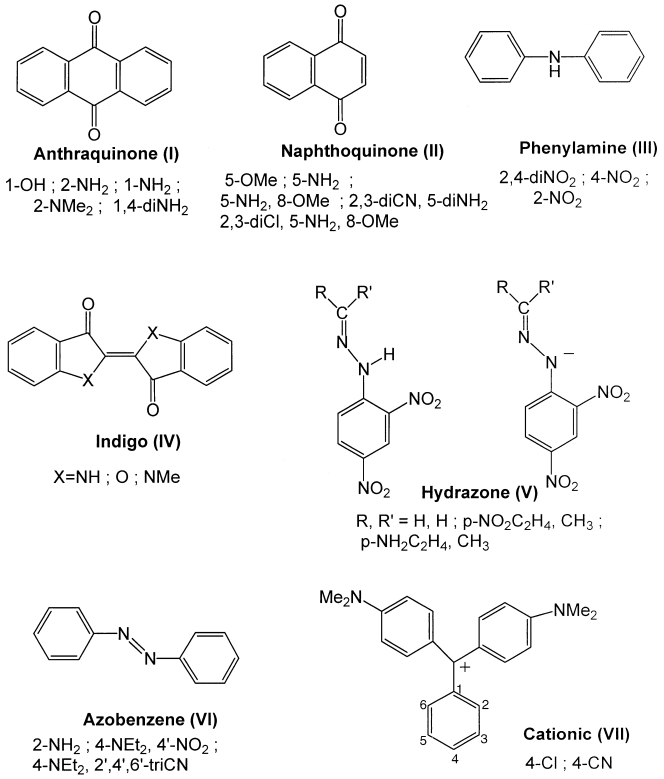

Fig. 1. Dyes studied in this work.

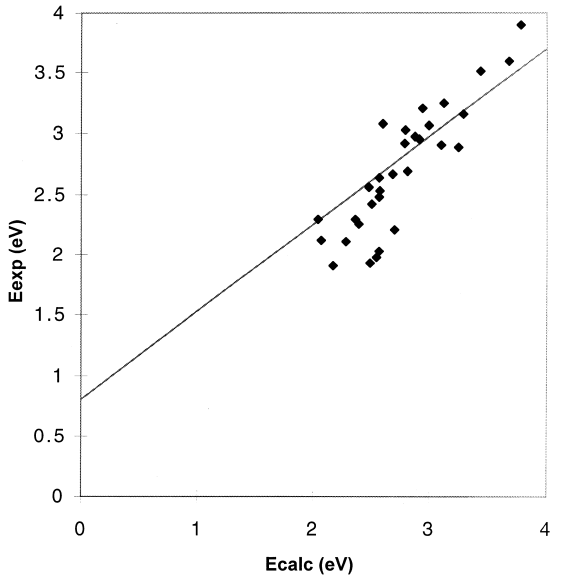

Fig. 2. Relation between experimental and calculated excitation energies corresponding to absorption maxima. Correlation coefficient $r = 0.88$.

dyes belonging to each family were first calculated using two different functionals, namely the hybrid B3LYP and the non-hybrid BPW91 [20], as well as three different Gaussian basis sets, 6-31G, 6-31G* and 6-31 + G*. In a second step, the TD-DFT absorption wavelengths and oscillator strengths for all the dyes were calculated.

Results presented in this paper were performed using DFT and TD-DFT programs implemented in Gaussian 98 [21].

3. Results and discussion

3.1. Effect of the functional and basis set on absorption wavelength

Table 1 gives the excitation energy differences between experimental data and the TD-DFT results obtained using the B3LYP and BPW91 functional and the 6-31G basis set. From

Table 1
Energy differences in eV between: (i) B3LYP and BPW91 transition energies: (ii) B3LYP and experimental transition energies: (iii) BPW91 and experimental transition energies with 6-31G basis set

Dyes	Substituents	B3LYP−BPW91	B3LYP−exp	BPW91−exp
Anthraquinone	1-NH_2	0.40	0.02	−0.38
dyes I	2-NH_2	0.55	−0.23	−0.78
	1,4-NH_2	0.25	0.14	−0.11
	2-NMe_2	0.53	−0.07	−0.60
	1-OH	0.44	−0.07	−0.51
Naphthoquinone	5-OMe	0.54	−0.27	−0.81
dyes II	2,3diCl, 5-NH_2, 8-OMe	0.27	0.07	−0.20
Phenylamine	2-NO_2	0.33	−0.13	−0.46
dyes III	4-NO_2	0.45	0.13	−0.32
Indigo	X = NH	0.31	0.23	−0.07
dyes IV	X = O	0.56	0.02	−0.54
	X = Me	0.26	0.26	0.00
Hydrazone	Anion R = R′ = H	0.21	0.37	−0.16
dyes V	R = *p*-$NO_2C_6H_4$, R′ = CH_3	0.56	−0.12	−0.68
Azobenzene	None	0.29	−0.12	−0.41
dyes VI	2-NH_2	0.38	−0.10	−0.48
	4-NEt_2, 2′,4′,6′-triCN	0.23	0.50	0.27
Cationic	None[a]	0.20	0.54	0.34
dyes VII		0.34	0.20	−0.14
	4-CN[a]	0.22	0.56	0.34
		0.36	0.16	−0.20
Mean absolute energy difference			0.21	0.37
Maximum energy difference			0.56	0.81

[a] Results corresponding to the two lowest absorption maxima.

Table 2
Calculated transition energies in eV with 6-31G and 6-31G* basis set and difference between the two[a]

Dyes	Substituents	6-31G	6-31G*	ΔE
Anthraquinone dyes II	2-NH_2	2.79	2.81	−0.02
	1,4-NH_2	2.39	2.35	0.04
Naphthoquinone dye II	5-OMe	2.94	2.95	−0.01
Phenylamine dyes III	2-NO_2	2.79	2.84	−0.05
Indigo dyes IV	X = NH	2.28	2.25	0.03
	X = O	2.97	2.91	0.06
	X = Me	2.17	2.16	0.01
Hydrazone dyes V	Anion R = R′ = H	3.25	3.29	−0.04
	R = *p*-$NO_2C_6H_4$ R′ = CH_3	3.12	3.15	−0.03
Azobenzene dyes VI	None	3.78	3.72	0.06
	2-NH_2	2.88	2.87	0.01
Cationic dye VII	4-NEt_2, 2′,4′,6′-triCN	2.70	2.68	0.02
		2.57	2.55	0.02

[a] Results obtained with B3LYP functional.

preliminary calculations (not reported here), we noted that the highest energy differences were obtained between a hybrid and non-hybrid functional. Excitation energies obtained with the non-hybrid BPW91 and BP86 functionals were very close, as were the results obtained using the hybrid B3LYP and B3PW91 functionals.

All excitation energies calculated using B3LYP are higher than those calculated using BPW91, by 0.21 to 0.56 eV. The mean difference between calculated and experimental excitation energies is 0.21 eV with the B3LYP functional and 0.37 eV with the BPW91 functional, with a maximum energy difference of 0.56 eV for B3LYP and 0.81 eV for BPW91. The best agreement with experiment is thus obtained with the B3LYP functional.

Three basis sets were used in the calculations, namely 6-31G, 6-31G* including polarization functions and 6-31 + G* including polarization and diffuse functions. The 6-31 + G* basis set is rather large and was used only for two hydrazone dyes which are anionic and for which diffuse functions could be necessary. Calculated absorption wavelengths are reported in Table 2 for the 6-31G* basis set and in Table 3 for the 6-31 + G* basis set.

Table 3
Calculated transition energies in eV with 6-31G and 6-31 + G* basis set and difference between the two[a]

Dyes	Substituents	6-31G	6-31 + G*	ΔE
Hydrazone dyes V	Anion R = R′ = H	3.25	3.13	0.12
	R = *p*-$NO_2C_6H_4$ Anion R′ = CH_3	2.81	2.72	0.09

[a] Results obtained with B3LYP functional.

For all the dyes, the energy differences between the 6-31G and 6-31G* basis are between 0.01 and 0.06 eV. This is very small and indicates that the addition of polarization functions does not bring any significant improvement to the calculation of excitation energies of these dyes. The energy differences between excitation energies obtained with 6-31G and 6-31 + G* for hydrazone dyes are 0.09 and 0.12 eV. These are still reasonable, considering the anionic nature of the dyes.

From these calculations, we conclude that the combination B3LYP/6-31G yields accurate results and will be used for all the dyes.

3.2. B3LYP/6-31G results for all the dyes

Table 4 lists the absorption wavelengths, oscillator strengths and absorption coefficients obtained for all the dyes of Fig. 1. Note that the computed values correspond to vertical energies and the relaxation effects of the excited dyes are not taken into account. The following points will be discussed; the ability of TD-DFT to reproduce absorption maxima, oscillator strengths and the spectral shifts observed within a family of dyes.

Table 4
Experimental and calculated absorption wavelengths λ_{max} (in nm) and oscillator strengths

	Experimental			TD-DFT		ΔE (eV)[a]
Dyes substituents	λ_{max}	log ϵ	f	λ_{max}	f	TD-DFT–exp.
Anthraquinone dyes I [23]						
1-OH	405	–	0.113	414	0.111	0.07
2-NH_2	410	–	0.091	444	0.033	0.23
1-NH_2	465	–	0.114	461	0.105	0.02
2-NMe_2	470	–	0.109	483	0.066	0.07
1,4-diNH_2	550	–	0.157	518	0.141	0.14
Naphthoquinone dyes II [24]						
5-OMe	387	3.56	0.063	422	0.064	0.27
5-NH2	484	3.73	0.093	500	0.072	0.08
5-NH2, 8-OMe	512	3.60	0.069	495	0.083	0.08
2,3-diCl, 5-NH_2, 8-OMe	540	3.80	0.109	525	0.113	0.07
2,3-diCN, 5-NH_2	585	3.61	0.070	599	0.068	0.05
Phenylamine dyes III [25]						
2,4-diNO_2	353	4.21	0.280	365	0.154	0.08
				361	0.195	
4- NO_2	393	4.43	0.465	377	0.374	0.13
2-NO_2	425	3.89	0.134	445	0.133	0.13
Indigo dyes IV [26–28]						
X = O	420	4.08	0.208	426	0.201	0.02
X = NH	605	4.22	0.287	543	0.197	0.23
	326	–	–	326	0.225	0.00
X = NMe	650	4.13	0.233	571	0.172	0.26
Hydrazone dyes V [29]						
Neutral R = R′ = H	345	4.32	0.361	337	0.342	0.09
R = *p*-$NO_2C_6H_4$, R′ = CH_3	382	4.54	0.599	397	0.543	0.12
R = *p*-$NH_2C_6H_4$, R′ = CH_3	403	4.43	0.465	477	0.379	0.48
		–	–	336	0.388	
Ionic R = R′ = H	430	4.24	0.300	382	0.358	0.36
	500	4.02	0.181	483	0.086	0.09
R = *p*-$NO_2C_6H_4$, R′ = CH_3	461	4.42	0.455	441	0.787	0.12
R = *p*-$NH_2C_6H_4$, R′ = CH_3	540	4.57	0.642	607	0.580	0.25
Azobenzene dyes VI [30–32]						
None	318	4.33	0.462	328	0.633	0.12
2-NH_2	417	3.8	0.109	431	0.248	0.10
4-NEt_2, 4′-NO_2	490	4.56	0.627	482	0.691	0.04
4-NEt_2, 2′,4′,6′-triCN	562	4.67	0.808	459	0.842	0.50
Cationic dyes VII [33–35]						
None	612	5.02	1.809	483	0.654	0.54
	427	4.30	0.345	400	0.295	0.20
4-Cl	627.5	4.91	1.405	487	0.645	0.57
				412	0.372	
4-CN	643	4.94	1.505	498	0.614	0.56
	429	4.20	0.274	406	0.378	0.16

[a] Energy difference between experimental and calculated transition energies (in eV). Calculated values obtained with 6-31G basis set and B3LYP functional.

3.2.1. Absorption wavelength

Overall the results are quite satisfactory. The TD-DFT method is able to predict transition energies to within a few tenths of an eV (Fig. 2). The mean difference between experimental and calculated excitation energies correspond to the absorption maximum (higher oscillator strength) which is 0.19 eV (38 nm), compared to 0.48 eV (75 nm) using the INDO/S method [5]. The energy differences between experimental and calculated values are less than 0.4 eV for all the dyes except for three cationic dyes, an azobenzene dye and a hydrazone dye.

For the cationic dyes, TD-DFT calculations give shorter absorption wavelength for the first absorption maximum (from 129 to 145 nm less than the experimental values), but reproduce correctly the second absorption maximum. Two explanations can be proposed. First, this absorption band of these dyes has a strong charge transfer character and the corresponding excited states have a large dipole moment. Such bands can be strongly affected by the solvent. Experimental values have been determined using CH_3COOH [33–35]. Second, the relaxation of the molecule in its excited state may be important. For the hydrazone dye, calculations give two absorption bands of equal intensity, whereas experimentally, only one absorption band is observed with a maximum between the two calculated bands. For the azobenzene dye substituted with cyano groups, the absorption wavelength is underestimated by the calculations, whereas TD-DFT gives correct values for other azobenzene dyes.

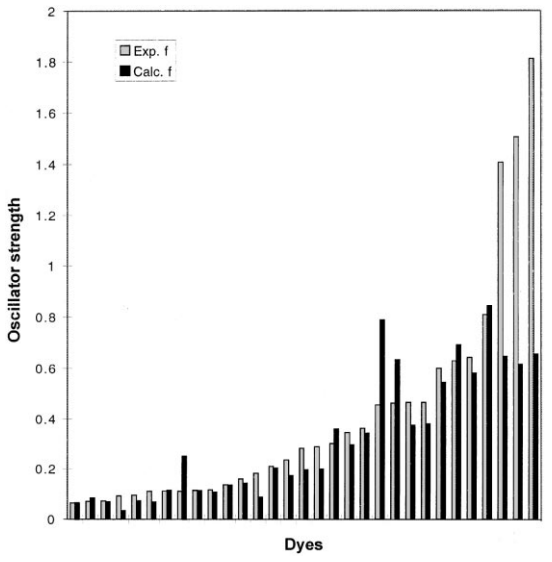

Fig. 3. Relation between experimental and calculated oscillator strengths.

3.2.2. Intensity of the absorption bands

Experimental absorption coefficients and calculated oscillator strengths are reported in Table 4. Experimental oscillator strengths were only available for anthraquinone dyes. However, in order to compare calculated and experimental values more directly, oscillator strengths were also determined from experimental absorption coefficients using the relation [22]:

$$f \cong 4.32 \times 10^{-9} \varepsilon_{max} \Delta\omega_{1/2} \quad (1)$$

where ϵ_{max} is the experimental absorption coefficient in l mol^{-1} cm^{-1} and $\Delta\omega_{1/2}$ corresponds to the halfwidth of the absorption band in cm^{-1}.

In the values reported in Table 4, $\Delta\omega_{1/2}$ was taken equal to 4000 cm^{-1} so that all the bands for all the dyes are supposed to have the same width. This is a crude approximation which simply means that absorption coefficients are scaled in order to compare them directly with calculated oscillator strengths.

However, for anthraquinone dyes, the oscillator strengths, which have been directly measured experimentally, are in very good agreement with the calculated values. Fig. 3 shows that the highest discrepancy is obtained for the first absorption band of the cationic dyes. Nevertheless, the very high values of f deduced from experimental values of ϵ ($f > 1.0$) for these dyes indicate that the actual experimental band width is larger than 4000 cm^{-1}; TD-DFT correctly predicts a very intense absorption. Overall, TD-DFT reproduces well the intensity of the absorption band of the dyes.

3.2.3. Spectral shift induced by a substituent

Another important aspect provided by the absorption wavelength calculation of dyes is a correct prediction of the spectral shift induced by a small change of the molecule. Fig. 4 gives the spectral shifts of dyes obtained within each family

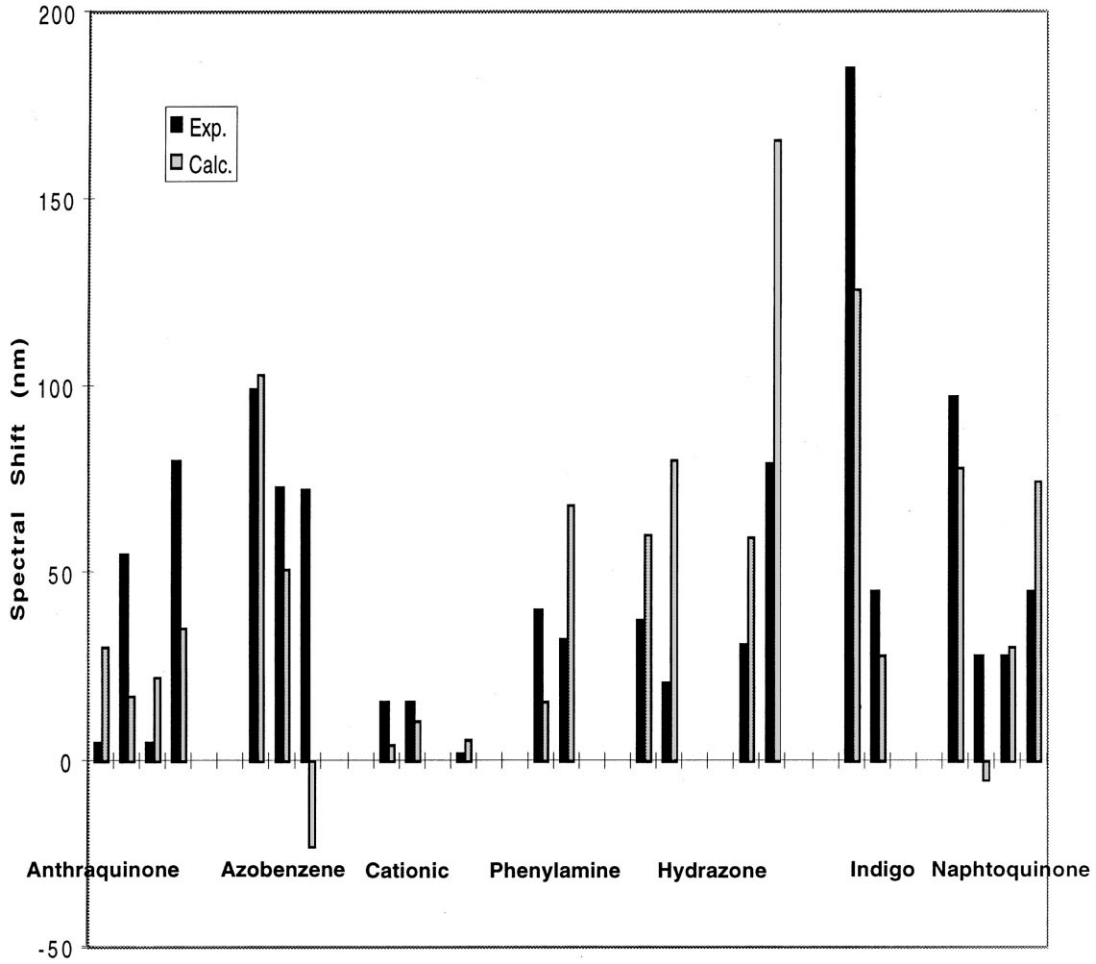

Fig. 4. Calculated and experimental spectral shift within each dye series, relative to the dye with the shortest absorption wavelength.

relative to the absorption maximum of the dye with the shortest absorption wavelength. From this diagram it is apparent that the sign of the spectral shift is correctly reproduced for all the dyes except for the azobenzene dye with cyano groups and for a naphthoquinone dye.

4. Conclusions

TD-DFT calculations using the B3LYP functional and the 6-31G basis set correctly reproduced the absorption wavelength, spectral shift and intensity of the bands. There are only a few cases for which calculations do not agree with experimental values.

When only a limited number of nuclear conformations are possible for a dye, the absorption wavelength can be predicted with good accuracy (see results for naphthoquinones, indigo, anthraquinones and phenylamine dyes). In contrast, when the dye is more flexible, the structure is more difficult to predict, the geometry of the excited molecule may largely differ from the molecule in its ground state, and the molecule in solution may exist in several conformations. The variation of

dihedral angles may strongly affect the aromaticity of the dye and the difference between experimental and calculated values becomes larger as noted for hydrazone, azobenzene and cationic dyes.

This study provides a benchmark calibration of the TDDFT method for large organic dyes used in industry. We believe that these data are important for the practical application of quantum chemistry in the design of functional dyes.

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