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REGULAR ARTICLE

On the TD-DFT UV/vis spectra accuracy: the azoalkanes

Denis Jacquemin · **Eric A. Perpète** · **Ilaria Ciofini** · **Carlo Adamo**

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Abstract Using an ab intio TD-DFT approach systematically accounting for the molecular surroundings effects, we have computed the $n \rightarrow \pi^{\star}$ absorption wavelength of 22 azoalkane derivatives. For the complete set of molecules, we propose a theoretical procedure able to reproduce the major auxochromic effects, and to deliver a mean absolute error of 5.8 nm (0.056 eV) with maximal deviations limited to 21 nm (0.20 eV). The impact of including in the model explicit solvent molecules is discussed as well. This contribution confirms that PCM-TD-PBE0 is a first-grade method for simulating the vertical absorption spectra of organic dyes.

Keywords Azoalkane · Azo derivatives · TD-DFT · Absorption spectra · $n \rightarrow \pi^{\star}$ transitions

1 Introduction

The time-dependent density functional theory (TD-DFT) originally developed 20 years ago by Runge and Gross [1,2], has become a widely used *ab initio* tool for theoretically evaluating excited state energies and more recently excited state geometries [3–6]. This popularity is due to TD-DFT's efficiency to rapidly provide transition energies for (monodeterminental) systems in both gas and condensed phases [7]. In contrast, the elaborated ab initio wavefunction approaches such as EOM-CC and CAS-PT2 are more computationally demanding. Consequently, they are often useable for simulating gas-phase experiments only, whereas most of the semiempiricial schemes, though still valuable to get first chemical insights or the main experimental trends, definitively lack of consistency. An extra TD-DFT advantage is that its limitations are now well understood. Indeed, in the framework of excited state studies, it tends to leave the tracks when charge separation takes place between distant moieties of the molecule [8,9], or for high-energy Rydberg states [10]. Note that such limitations can be partly corrected using range-separated hybrids, and are thus more related to the functional technology than to the TD-DFT theory itself [11–16]. In short, when conventional hybrids are used the TD-DFT UV/vis spectra often agree with experiment for compounds characterised by a well-defined chromophoric unit, mainly centred on a few atoms [17–19]. On the contrary, it might fail for large biological complexes [9] or cyanine derivatives [20,21]. In that latter case, CAS-PT2 is required to reproduce the qualitative evolution of the absorption wavelength: the longer the chain, the stronger the multi-determinental nature [22].

Professor Nino Russo and his co-workers have been extremely active in tailoring, improving and using TD-DFT tools for a large panel of chemical and practical applications [23–27]. For instance, new transition-metal texaphyrin complexes containing boron and various metals have been recently designed in order to improve their activity within the scope of photo-dynamic therapy [25,27]. Russo et al. have

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D. Jacquemin, E. A. Perpète are research associates of the Belgian National Fund for Scientific Research.

D. Jacquemin (✉) · E. A. Perpète
Laboratoire de Chimie Théorique Appliquée,
Groupe de Chimie Physique, Théorique et Structurale,
Facultés Universitaires Notre-Dame de la Paix,
rue de Bruxelles, 61, 5000 Namur, Belgium
e-mail: denis.jacquemin@fundp.ac.be

I. Ciofini · C. Adamo (✉)
Ecole Nationale Supérieure de Chimie de Paris,
Laboratoire Electrochimie et Chimie Analytique,
UMR CNRS-ENSCP no. 7575, 11, rue Pierre et Marie Curie,
75321 Paris Cedex 05, France
e-mail: carlo-adamo@enscp.fr

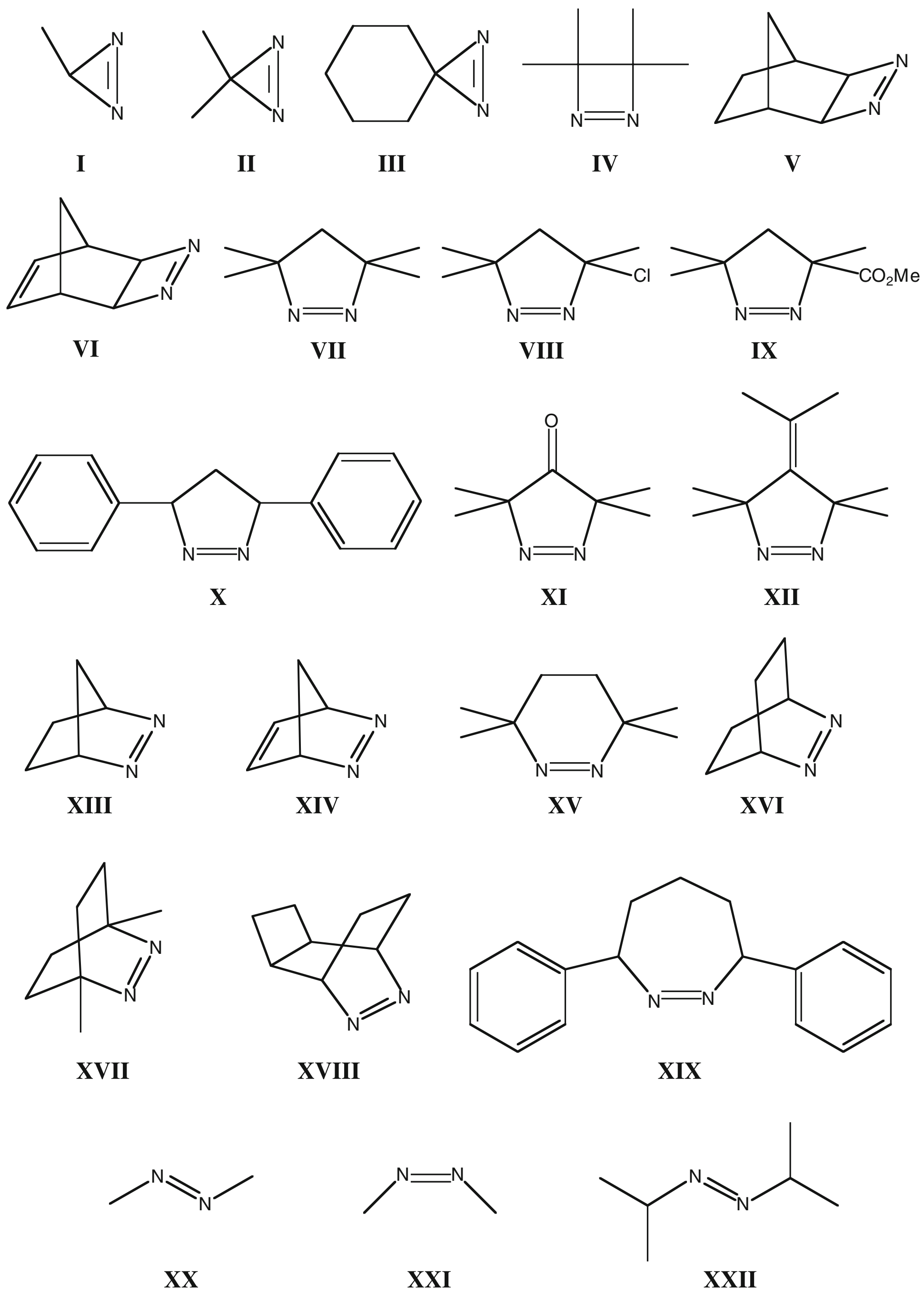

Fig. 1 Sketch of the cyclic (**I**–**XIX**) and non-cyclic (**XX**–**XXII**) azoalkanes investigated

notably assessed the accuracy of TD-DFT for computing the Q-like band of these complexes, as this absorption plays a major role in the drug-design of these photosensitizers.

In this study, we focus on the $n \rightarrow \pi^\star$ transition of azoalkane derivatives. According to Ref. [28], there are only three major type of "real-life" $n \rightarrow \pi^\star$ chromophores: the thiocarbonyl compounds ($R_{1,2}C{=}S$), the nitroso dyes (R–N=O), and the azo systems (R_1–N=N–R_2). The two first series have already received extensive TD-DFT treatments, and we refer the reader to Refs. [29,30] and [31] for the thiocarbonyl and nitroso chromophores, respectively. The azobenzenes (AB) are probably the most relevant representatives of the azo class, and they have been the subject of several TD-DFT investigations [20,32–36], though in most AB the $n \rightarrow \pi^\star$ transition is hidden by a strongly dipole-allowed $\pi \rightarrow \pi^\star$ band. Consequently, the availability of accurate experimental AB $n \rightarrow \pi^\star$ energies is sparse. In the present work, we have therefore focussed on cyclic and non-cyclic azoalkanes (Fig. 1) that present a well-resolved experimental $n \rightarrow \pi^\star$ band, and, to the best of our knowledge, have never been theoretically characterised with modern TD-DFT tools.

2 Methodology

All simulations have been performed with the Gaussian03 suite of programs [37], with a tighten self-consistent field convergence threshold (10^{-8} a.u.). To perform our computations, we have followed a well-established three-step approach [19,38,39]: (1) the ground-state geometries have been optimised until the residual mean force is smaller than 1.0×10^{-5} a.u.; (2) the vibrational spectra are analytically determined to confirm that structures are actual minima; and (3) the vertical transition energies to the valence excited states are computed with TD-DFT.

The ground-state properties are evaluated with the triple-ζ 6-311G(d,p) basis set (BS) using the B3LYP functional [40, 41]. This combination is backed by previous investigations that, one the one hand, have shown that 6-311G(d,p) provides converged geometrical parameters for numerous organic compounds [42–44] and, on the other hand, demonstrated that B3LYP is especially adequate to determine the N=N bond length of AB [35,36]. The electronic excitations were evaluated with the parameter-free hybrid PBE0 functional [45,46] and the 6-311+G(d,p) BS. PBE0 has indeed proved its efficiency to evaluate the absorption spectrum of organic dyes [19,25,38,39,47–49] and azo derivatives λ_{max} does not vary when computed with 6-311+G(d,p) or larger BS [35]. Similarly the simulation of $n \rightarrow \pi^\star$ transitions is not improved (nor worsen) by the use of range-separated hybrids [50], easing the use of conventional hybrids in the present investigation.

At each stage, including the geometry optimisation and Hessian calculations, the bulk solvent effects are evaluated by means of the polarisable continuum model (PCM) [7,51]. In PCM, one divides the problem into a solute part (the azoalkane) lying inside a cavity, and a solvent part represented as a structure-less material, characterised by its macroscopic properties. PCM is able to obtain a valid approximation of solvent effects as long as no specific interactions link the solute and the solvent molecules. For this reason, we have selected aprotic solvents if experimental measurements have been performed in various media [52]. Because we study UV/vis spectra, we have selected the non-equilibrium PCM solutions [7], since the absorption processes typically present short characteristic times.

3 Results and discussion

The theoretical and experimental absorption wavelengths are compared in Table 1, and the corresponding vertical transition energies are sketched in Fig. 2. Note that for two of the cyclic derivatives (**XV** and **XVI**), we found slightly different experimental values in the literature, and the average is used in our comparisons. Let us also underline that for **I** and **II**, the measurements correspond to the 0–0 transition rather than to a (strictly) vertical absorption. As can be seen in Table 1 and Fig. 2, there is a nice agreement between the theoretical and experimental λ_{max} for both cyclic and non-cyclic azoalkanes. In the former, the stress implied by the cycle has a crucial importance for determining the λ_{max}, that reaches a minimum for five-member rings. This is confirmed by investigating the analogous **II**→**IV**→**VII** →**XV**→**XIX** series, for which the experiment initially shows hypsochromic displacements, followed by bathochromic shifts with successive increments of −11, −20, +55 and +8 nm. This effect is almost quantitatively reproduced by TD-DFT that yields −4, −21, +60 and +16 nm. Likewise, the measured spectral difference between **XIII** and **XVI** (+37 nm) is correctly

Table 1 Comparison between the measured and calculated absorption wavelength of the first $n \rightarrow \pi^\star$ transition (nm)

Compound	Solvent	Theory	Experiment	$\lvert\Delta\lambda\rvert$	Reference
I	Gas	336	342	6	[55]
II	Gas	354	358	4	[56]
III	Alk.	362	366	4	[52]
IV	Alk.	350	347	3	[57]
V	Alk.	354	353	1	[52]
VI	Alk.	351	354	3	[52]
VII	Alk.	329	327	2	[57]
VIII	Alk.	342	332	10	[52]
IX	Alk.	329	327	2	[52]
X	EtOH	328	329	1	[58]
XI	Alk.	367	357	10	[52]
XII	Alk.	329	327	2	[52]
XIII	Gas	339	339	0	[59]
	Alk.	340	341	1	[52]
XIV	Alk.	329	342	13	[60]
XV	Alk.	389	383, 380	7	[57,61]
XVI	Gas	381	376	5	[59]
	Alk.	382	378, 377	4	[52,61]
XVII	Alk.	389	383	6	[52]
XVIII	Alk.	388	383	5	[52]
XIX	$CHCl_3$	405	390	15	[58]
XX	Water	352	343	9	[62]
XXI	Water	374	353	21	[62]
XXII	Gas	357	362	5	[63]
MAE				6	

All theoretical results have been obtained with the PCM-TD-PBE0/6-311+G(d,p)//PCM-B3LYP/6-311G(d,p) approach, but for gas-phase value for which the PCM model was not included. $\lvert\Delta\lambda\rvert$ indicates the absolute difference between experiment and theory (in nm)

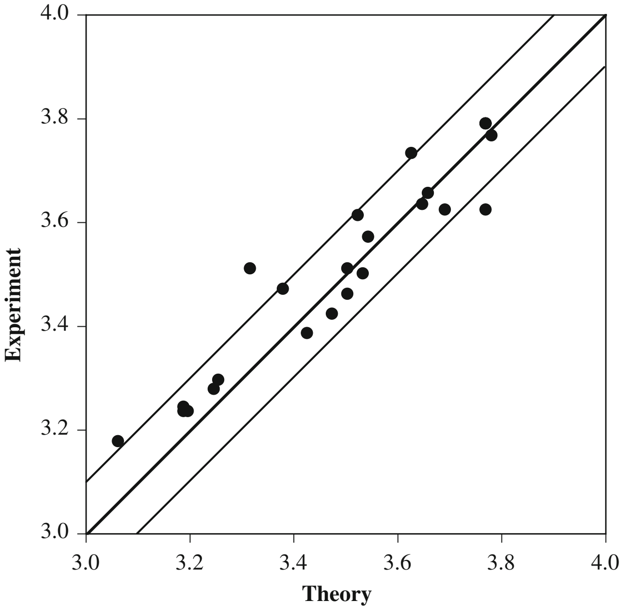

Fig. 2 Comparison between theoretical and experimental transition energies in eV. The *central line* indicates a perfect match, whereas the *two side lines* are borders of ±0.1 eV deviation

estimated by TD-DFT (+42 nm). The *trans–cis* isomerism in azomethane is associated with a bathochromic displacement that we overestimate, partly due to the lack of specific solute–solvent effects in our model (see below). In addition, TD-DFT appropriately models more "standard" auxochromic effects. Indeed, on the one hand, replacing the ketone in **XI** by an alkene unit, provokes an experimental (theoretical) −30 nm (−38 nm) hypsochromic displacement, and, on the other hand, adding side methyl groups to **XVI** leads to small bathochromic displacements in both experiment (+5 nm) and theory (+7 nm). Finally, for **XIII** and **XVI** the positive solvatochromic effect observed between gas-phase and alkane environment is correctly predicted by the PCM model.

A statistical analysis of the data of Table 1 gives a mean signed error (MSE = experiment-theory) of −2.8 nm and a mean absolute error (MAE) of 5.8 nm, becoming MSE = 0.023 eV and MAE = 0.056 eV, on the energetic scale. Impressively, the maximal absolute deviations are limited to 21 nm (0.20 eV), with only 3 (5) cases for which the errors exceeds 10 nm (0.10 eV). Consistently, the R^2 obtained by simple linear regression is larger than 0.9 in both the wavelength and energetic scales. Actually, statistically treating (i.e. fitting to the experimental results) our theoretical values would only slide the MAE to 0.047 eV. For comparison purpose, similar average discrepancies have been obtained for the $n \rightarrow \pi^\star$ transitions of nitroso derivatives (MAE = 0.050 eV, with PBE0) [31] and thiocarbonyl dyes (MAE = 0.074 eV, with B3LYP) [30]. This confirms that TD-DFT is especially well suited for studying this type of localised excitations. For the $\pi \rightarrow \pi^\star$ transition energies of 100+ organic dyes, we recently obtained (with a very similar computational procedure) a MAE of 0.14 eV [53], and in any case these errors are much smaller than the usual expected accuracy of TD-DFT (0.2–0.3 eV). Indeed, previous studies based on a wide panel of compounds but lacking environmental effects and relying on smaller atomic basis sets, respectively attained MAE of 0.29 and 0.24 eV for $\pi \rightarrow \pi^\star$ transitions in sulphur-free and sulphur-bearing molecules [21,29], as well as 0.19 eV for another large set of dyes [20].

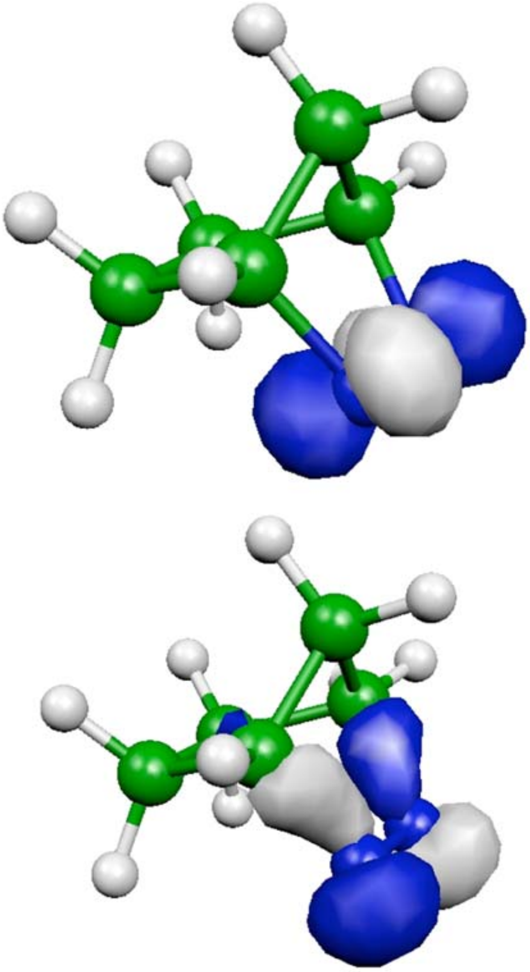

Fig. 3 HOMO (*bottom*) and LUMO (*top*) of **XIII** in gas-phase. These orbitals have been obtained with PBE0/6-311+G(d,p) and acontour threshold = 0.10 a.u

The $n \rightarrow \pi^\star$ transition typically corresponds to the first singlet excitation, and implies both the HOMO and LUMO of the azoalkanes. For **XIII**, these frontier orbitals are sketched in Fig. 3 and, without surprise, the excitation is obviously localised on the two nitrogen atoms. Subsequently, we have assessed the adequacy of the N=N bond length as a molecular descriptor of the $\lambda_{\max}$. Unfortunately, there is no strong correlation between this distance and the transition energies: the linear R^2 is 0.07! In fact, the N=N bond length better correlates with the ring size (i.e. number of atoms involved in

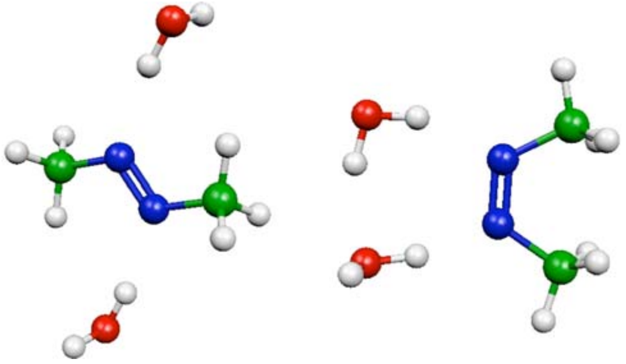

Fig. 4 Optimised geometries for the azomethane–(water)$_2$ cluster in *trans* (*left*) and *cis* (*right*) conformations. These structures have been determined with the PCM(water)-B3LYP/6-311G(d,p) approach

the azo ring): 1.226 ± 0.002 Å for three-member rings, 1.260 ± 0.002 Å for four-member rings, 1.235 ± 0.006 Å for five-member rings and 1.240 ± 0.006 Å for six-member rings. Within this subgroups, we observe that, in general the longer the diazo double bond, the larger the computed $\lambda_{\max}$, as could be expected for a transition towards a $\pi^\star$ orbital. However, exceptions do exist, like **XV** that possesses both relatively small transition energy, and N=N distance. In short, the double bond length cannot be easily used to predict the $\lambda_{\max}$ of azoalkane dyes, contrary to what we found for thiodinigoïds [19].

Our largest PCM-TD-DFT error appears to the *cis*-azomethane (**XXI**), and the theory-experiment discrepancy for *trans*-azomethane (**XX**) is 1.5 times larger than the average deviation. Parts of these errors originate in the hydrogen bonds water can form with the nitrogen lone pairs. Such intermolecular interactions could stabilise the *n* orbital and lead to an increase of the transition energy, but PCM is unable to take them into account. For the records, we have therefore optimised azomethane-(water)$_2$ complexes for both isomers (Fig. 4). For the $\lambda_{\max}$ of the *cis* derivative, we observe systematic hypsochromic displacements when including solvent effects. Indeed, starting with the 328 nm $\lambda_{\max}$ in gas-phase, we compute 374 nm with a bulk solvent environment, 367 nm with two explicit water molecules and 360 nm when both medium effects are accounted for. This last value is much closer to the experimental data (353 nm). Similar (though smaller) modifications are noted for the *trans* conformer, with a $\lambda_{\max}$ of 355 nm in gas-phase, 352 nm with the PCM model, 352 nm for the water-cluster and 346 nm for the full model. The latter value being on the experimental spot of 343 nm. Therefore, adding two explicit water molecules to our model azomethane allows to divide the theory–experiment discrepancy by a factor of three, and to reach a more accurate picture for the impact of isomerisation. In that sense, some of the largest errors noted in Table 1 should be directly attributed to the lack of explicit solute-solvent hydrogen bonds.

4 Conclusions and outlook

The $\lambda_{\max}$ of a series of cyclic and non-cyclic azoalkanes have been computed using a PCM-TD-PBE0/6-311+G(d,p)//PCM-B3LYP/6-311G(d,p) approach. It turns out that such a procedure is able to accurately foresee the main solvatochromic and auxochromic effects. For the latter, both the impact of substitution and the modification of the ring stress are indeed correctly predicted. Of course, a better accuracy can only be reached in a protic medium by including explicit solvent molecules in the theoretical model. For the 24 treated cases, we obtained a MSE of −2.8 nm (0.023 eV) and a MAE of 5.8 nm (0.056 eV), with only 3 (5) molecules presenting errors above 10 nm (0.10 eV). As these errors are much smaller than the $\pi \rightarrow \pi^\star$ counterpart(s), this study demonstrates once again that PCM-TD-PBE0 is a fast and reliable method for calculating $n \rightarrow \pi^\star$ absorption bands.

We are currently investigating the fluorescence of several azo derivatives in order to assess the transferability of our model to the emission phenomena.

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References

1. Runge E, Gross EKU (1984) Phys Rev Lett 52:997
2. Burke K, Werschnik J, Gross EKU (2005) J Chem Phys 123:062206
3. van Caillie C, Amos RD (1999) Chem Phys Lett 308:249
4. van Caillie C, Amos RD (2000) Chem Phys Lett 317:159
5. Furche F, Ahlrichs R (2002) J Chem Phys 117:7433
6. Jacquemin D, Perpète EA, Scalmani G, Frisch MJ, Assfeld X, Ciofini I, Adamo C (2006) J Chem Phys 125:164324
7. Cossi M, Barone V (2001) J Chem Phys 115:4708
8. Tozer DJ (2003) J Chem Phys 119:12697
9. Dreuw A, Head-Gordon M (2004) J Am Chem Soc 126:4007
10. Ciofini I, Adamo C (2007) J Phys Chem A 111:5549
11. Tawada T, Tsuneda T, Yanagisawa S, Yanai T, Hirao K (2004) J Chem Phys 120:8425
12. Rudberg E, Salek P, Helgaker T, Agren H (2005) J Chem Phys 123:184108
13. Chiba M, Tsuneda T, Hirao K (2006) J Chem Phys 124:144106
14. Cai ZL, Crossley MJ, Reimers JR, Kobayashi R, Amos RD (2006) J Phys Chem B 110:15624
15. Vydrov OA, Scuseria GE (2006) J Chem Phys 125:234109
16. Peach MJG, Cohen AJ, Tozer DJ (2006) Phys Chem Chem Phys 8:4543
17. Jacquemin D, Preat J, Perpète EA (2005) Chem Phys Lett 410:254

18. Jacquemin D, Preat J, Wathelet V, Perpète EA (2006) J Chem Phys 124:074104
19. Jacquemin D, Preat J, Wathelet V, Fontaine M, Perpète EA (2006) J Am Chem Soc 128:2072
20. Guillaumont D, Nakamura S (2000) Dyes Pigm 46:85
21. Fabian J (2001) Theor Chem Acc 106:199
22. Schreiber M, Bub V, Fülscher MP (2001) Phys Chem Chem Phys 3:3906
23. Petit L, Adamo C, Russo N (2005) J Phys Chem B 109:12214
24. Petit L, Quartarolo A, Adamo C, Russo N (2006) J Phys Chem B 110:2398
25. Quartarolo AD, Russo N, Sicilia E (2006) Chem Eur J 12:6797
26. Leopoldini M, Russo N, Chiodo S, Toscano M (2006) J Agr Food Chem 54:6343
27. Quartarolo AD, Russo N, Sicilia E, Lelj F (2007) J Chem Theory Comput 3:860
28. Griffiths J (1976) Colour and constitution of organic molecules. Academic Press, London
29. Fabian J, Diaz LA, Seifert G, Niehaus T (2002) J Mol Struct (THEOCHEM) 594:41
30. Jacquemin D, Wathelet V, Perpète EA (2006) J Phys Chem A 110:9145
31. Jacquemin D, Perpète EA (2006) Chem Phys Lett 420:529
32. Fliegl H, Köhn A, Hättig C, Ahlrichs R (2003) J Am Chem Soc 125:9821
33. Chen PC, Chieh YC, Wu JC (2005) J Mol Struct (THEOCHEM) 715:183
34. Liu JN, Yuan SF, Chen ZR (2005) J Mol Struct (THEOCHEM) 730:151
35. Briquet L, Vercauteren DP, Perpète EA, Jacquemin D (2006) Chem Phys Lett 417:190
36. Briquet L, Vercauteren DP, André JM, Perpète EA, Jacquemin D (2007) Chem Phys Lett 435:257
37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C.02. Gaussian, Wallingford
38. Perpète EA, Wathelet V, Preat J, Lambert C, Jacquemin D (2006) J Chem Theory Comput 2:434
39. Jacquemin D, Bouhy M, Perpète EA (2006) J Chem Phys 124:204321
40. Becke AD (1993) J Chem Phys 98:5648
41. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623
42. Adamo C, Scuseria GE, Barone V (1999) J Chem Phys 111:2889
43. Curtiss LA, Raghavachari K, Referm PC, Pople JA (1997) Chem Phys Lett 270:419
44. Barone V, Adamo C (1996) J Chem Phys 105:11007
45. Adamo C, Barone V (1999) J Chem Phys 110:6158
46. Ernzerhof M, Scuseria GE (1999) J Chem Phys 110:5029
47. Pezzella A, Panzella L, Crescenzi O, Napolitano A, Navaratman S, Edge R, Land E, Barone V, d'Ischia M (2006) J Am Chem Soc 128:15490
48. Santoro F, Improta R, Lami A, Bloino J, Barone V (2007) J Chem Phys 126:084509
49. Improta R, Barone V, Santoro F (2007) Angew Chem Int Ed Engl 46:405
50. Jacquemin D, Perpète EA, Vydrov OA, Scuseria GE, Adamo C (2007) J Chem Phys 127:094102
51. Tomasi J, Mennucci B, Cammi R (2005) Chem Rev 105:2999
52. Mirbach MJ, Liu KC, Mirbach MF, Cherry WR, Turro NJ, Engel PS (1978) J Am Chem Soc 100:5122
53. Jacquemin D, Perpète EA, Scuseria GE, Ciofini I, Adamo C (2008) J Chem Theory Comput 4:123
54. Nguyen KA, Kennel J, Pachter R (2002) J Chem Phys 117:7128
55. Robertson LC, Merritt JA (1972) J Chem Phys 57:941
56. Robertson LC, Merritt JA (1972) J Chem Phys 57:2919
57. Engel PS, Hayes RA, Keifer L, Szilagyi S, Tomberlake JW (1978) J Am Chem Soc 100:1876
58. Overberger CG, Anselme JP, Hall JR (1963) J Am Chem Soc 85:2752
59. Solomon BS, Thomas TF, Steel C (1968) J Am Chem Soc 90:2249
60. Cohen SG, Zand R, Steel C (1961) J Am Chem Soc 83:2895
61. Cohen SG, Zand R (1962) J Am Chem Soc 84:586
62. Hutton RF, Steel C (1964) J Am Chem Soc 86:745
63. Robin MB, Simpson WT (1962) J Chem Phys 36:580