Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 410 (2005) 254–259

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

A TD-DFT study of the absorption spectra of fast dye salts

Denis Jacquemin *,1, Julien Preat, Eric A. Perpète 1

Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles, 61, B-5000 Namur, Belgium

Received 6 April 2005; in final form 28 April 2005
Available online 15 June 2005

Abstract

The UV/visible spectra of a series of diazonium (N_2^+) fast dyes have been evaluated by using a time-dependent density functional theory approach explicitly taking into account bulk solvation effects. Using the PBE0 functional with the 6-311G(2d,2p) atomic basis set, the agreement between theory and experiment is excellent for these cationic species. The effects on the spectra of chemical substitution are analysed.

1. Introduction

Fast dye salts are characterized by a diazonium (N_2^+) group bonded to an aromatic ring. These stable salts are highly soluble in water and are of primary importance in tinctorial industry due to their ability to form links with various fibers (cotton, silk, polyamide, etc.), once appropriate coupling components, such as napthol derivatives, are used to pad the textile being dyed [1,2]. This allows the in situ formation of diazo dyes which are often poorly soluble in water. In addition, small structural changes on the salt generally result in large shade/colour shifts for the dyed material. These properties make diazonium derivatives useful in several applied fields such as detecting dental caries lesions [3], colouring inorganic polymers [4], analyzing bilirubin in serum [5], etc.

This work aims at predicting and rationalizing the $\lambda_{\max}$ of a series fast dyes diazonium derivatives (Fig. 1). Nowadays, the molecular modelisation techniques offer a competitive alternative for the interpretation of experimental data arising from industrial interest and applications. The accurate prediction of UV/VIS spectra of large molecules is still a domain of concern [6], as semi-empirical methods, though especially tailored for, often woolly reproduce spectral patterns or trends. On the contrary, time-dependent density functional theory (TD-DFT) [7], is often found to be a robust and accurate method for low-lying excited states [8–10], and has been thoroughly applied to solve countless (bio-)-chemical and physical problems [11–18]. A limited number of TD-DFT investigations have been carried out on charged/radical species [19–30]: to our knowledge, only one recent work indirectly considers solvation effects in the study of the excitation spectra of non-neutral dyes [30].

2. Computational details

The calculations have been performed with the GAUSSIAN 03 [31] program, using a two-step procedure.

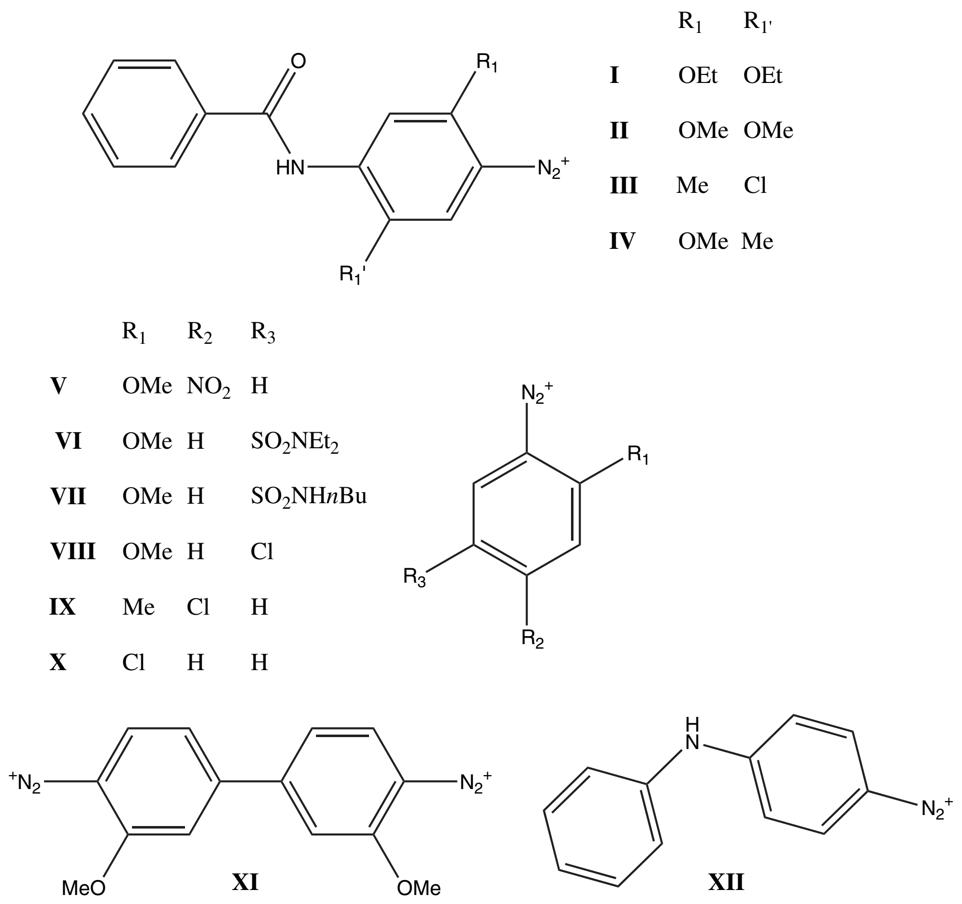
First, for each molecule, the ground-state geometry has been optimised with a TIGHT threshold on residual forces. It turned out that Adamo and Barone's hybrid PBE0 functional [32] combined with Pople's split-valence triple-ζ doubly polarised atomic basis set,

---

[*] Corresponding author. Fax: +32 81724567.
E-mail addresses: denis.jacquemin@fundp.ac.be (D. Jacquemin), eric.perpete@fundp.ac.be (E.A. Perpète).
URL: http://perso.fundp.ac.be/~jacquemd (D. Jacquemin).

[1] Research Associate of the Belgian National Fund for Scientific Research.

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.05.081



	R_1	$R_{1'}$
I	OEt	OEt
II	OMe	OMe
III	Me	Cl
IV	OMe	Me

	R_1	R_2	R_3
V	OMe	NO_2	H
VI	OMe	H	SO_2NEt_2
VII	OMe	H	SO_2NH*n*Bu
VIII	OMe	H	Cl
IX	Me	Cl	H
X	Cl	H	H

XI

XII

Fig. 1. Chemical structures of the investigated fast dyes.

6-311G(2d,2p), provides adequate results (see the following section). In PBE0, the percentage of exact, i.e., Hartree–Fock (HF), exchange amounts to 25%. After each optimisation, the vibrational spectra has been determined in order to verify that no imaginary frequency is found.

After the ground-state optimisation, the excitation spectrum of each molecule has been computed with TD-DFT, using the same 6-311G(2d,2p) basis set and the PBE0 functional. The excitations responsible for the colour of diazonium derivatives present a $\pi \rightarrow \pi^*$ character. Numerous extra functionals have been tested (see the following section). During the TD-DFT calculations, the bulk solvent effects are taken care off by means of the polarizable continuum model (PCM) [33,12]. In PCM, one divides the problem into a solute part (the fast dye salt) lying inside a cavity, and a solvent part (in our case, water or methanol) represented as a structureless material, characterized by its dielectric constant as well as other macroscopic parameters. PCM is able to obtain a valid approximation of solvent effects as long as there is no specific interaction, such as hydrogen bonds, between the solute and the solvent. In the experiments, the salts are constituted of the investigated cationic dye (Fig. 1), a counterion (often Cl^-) and sometimes additional $ZnCl_2$, remaining from the original diazonium preparation reaction. We have neglected the anions and zinc chloride in this Letter. Indeed, it is reasonable to state that once water-solvated, these ions will not affect the spectra of the cationic dye. This is confirmed by the experimental λ_{max} of **V** which is 375 nm independently of the counter-ion nature (BF_4^- or deprotonated 1,5-naphthalenedisulfonic acid) [2]. In this Letter, we have selected the so-called non-equilibrium PCM solutions, as we study an absorption process [12]. Except when noted the reported λ_{max} correspond to the transition energy of the first dipole-allowed excited state.

3. Methodological study

In Table 1, the λ_{max} of **X** has been computed using several levels of theory. This dye has been chosen since its small size, on the one hand, allows extensive computational investigation and, on the other hand, is expected to show a significant methodological sensitivity. For water-solvated **X** the experimental λ_{max} is 324 nm [2].