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# Theoretical Study of Photochromic Compounds. 1. Bond Length Alternation and Absorption Spectra for the Open and Closed Forms of 29 Diarylethene Derivatives

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We apply several exchange–correlation functionals in combination with time-dependent density functional theory to predict the maximum wavelengths in the absorption spectra for 29 diarylethene derivatives in both open and closed isomeric forms. Solvent effects and accurate molecular geometries are found to be important to obtain good agreement with experimental absorption wavelengths. In order to evaluate the quality of geometry optimization, we compare predicted bond length alternation parameters with experimental ones. We find the TD-M05/6-31G\*/PCM//M05-2x/6-31G\*/PCM theory level to give the best predictions for the structural and spectral parameters of the diarylethene derivatives. Applications of the photochromic diarylethene compounds as materials for optical switching and data storage based on their photocyclization properties are also discussed.

## 1. Introduction

Photochromism is a light-induced reversible molecular transition between two isomers, closed and open, with different absorption spectra. Apart from the color, the two isomers also differ in various physical and chemical properties such as refractive indexes, dielectric constants, oxidation–reduction potentials, and molecular geometry. The ultrafast changes in these properties upon photoirradiation can be used in various optoelectronic devices such as optical memory, optical switching, displays, and nonlinear optics. Irie and Lehn<sup>1–9</sup> were among the first authors to investigate diarylethenes as potential candidates for photochromic applications (Figure 1).

In the case of diarylethenes, the open form has a twisted  $\pi$ -system with conjugation between the two aromatic rings and is colorless, while the closed form has a nearly planar  $\pi$ -system and is colored. The distinct difference of the absorption maxima for the open and closed forms determines their color difference and has been attributed to the length of the conjugated chain. An important geometrical parameter of any conjugated system is the bond length alternation (BLA), defined as the difference between the lengths of the single and double bonds. For linear chain oligomers, it has been shown that the band gap, nonlinear optical (NLO) properties, excitation energies, and so forth strongly depend on BLA.<sup>10–15</sup> Thus, accurate description of the ground-state geometry is essential to predict the optical properties of photochromic diarylethenes.

Theoretical predictions of BLA for several series of conjugated oligomers were conducted by Jacquemin and co-workers in the past decade.<sup>16–23</sup> They performed ab initio calculations mainly on acyclic conjugated systems and concluded that (1) MP2 values are in good agreement with higher-order electron-correlated wave function approaches that include triple excitations, (2) basis set effects are relatively limited, and a polarized double- $\zeta$  basis is sufficient, at least for DFT calculations, (3) all conventional GGA and meta-GGA provide similar BLAs,

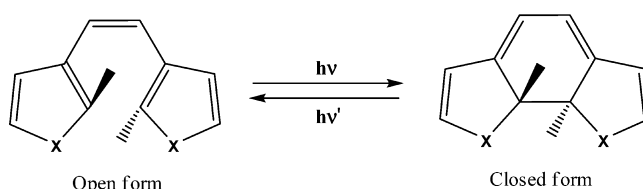


Figure 1. Photochromic diarylethene compounds (X = S, O, and Se).

which are much too small and too rapidly decreasing with chain length, (4) hybrid functionals correct this trends but to a small extent so that quantitative agreement with MP2 values is still far away, (5) conformation differences do not alter these three latter conclusions, and (6) self-interaction corrections included via the averaged density self-interaction correction (ADSIC) scheme improves BLA evolution obtained by conventional DFT approaches. For medium-size oligomers, ADSIC predicts BLA in better agreement with MP2 than B3LYP or PBE0. However, diarylethene derivatives have not been investigated in that respect.

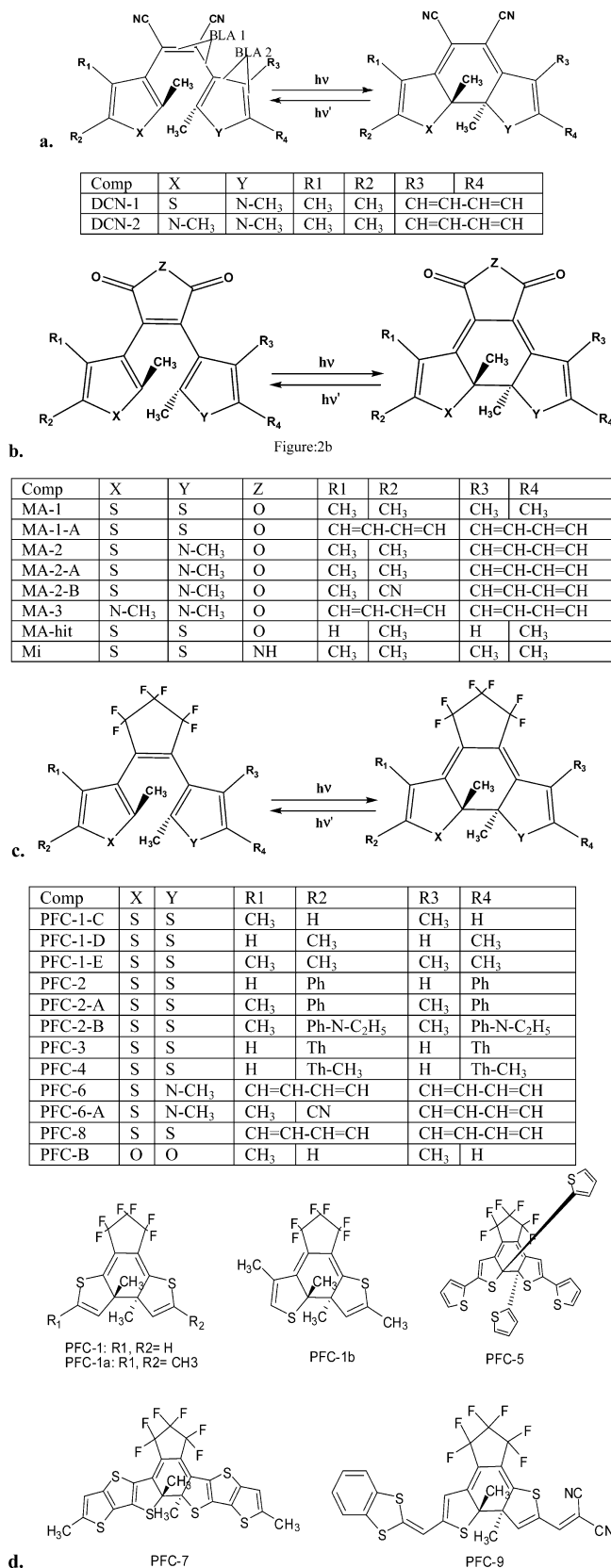
Recently, Nakamura et al.<sup>1</sup> reviewed theoretical studies of photochromic systems with the aim of understanding experimental spectroscopic data (NMR, Raman, IR, and ESR). They did not consider the UV–vis spectra, however. The visible spectra of the closed ring structures were predicted by Uchida et al.<sup>24</sup> using semiempirical methods, which lack accuracy. Majumdar et al. investigated dithienylethene derivatives as potential nonlinear optical (NLO) photoswitches, using DFT and time-dependent DFT (TD-DFT) calculations.<sup>25</sup> They studied the open and closed structures, stability, electronic absorption spectra, and hyperpolarizabilities. This pioneering DFT study was followed by others. Jacquemin, Perpete, et al. investigated several sets of closed ring isomers of dithienylethenes and found that a TD-DFT treatment gives much more accurate results than a semiempirical approach.<sup>17,18,20,21,26</sup> Similar studies were extended to both closed and open ring isomers.<sup>23,27,28</sup> Theoretical investigations of thermally irreversible photochromic systems have also been conducted by other groups in order to predict important ground-state properties.<sup>25,26,29,30</sup>

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**Figure 2.** (a,b) Benchmark set of open and closed ring isomers studied in this work, dicyano (DCN), maleicanhydride (MA), and maleimide (Mi) derivatives. (c,d) Perfluorocyclopentene derivatives (PFC).

The distinctive absorption spectra of the two isomeric forms of the photochromic compounds is an essential property to study. Experimental absorption spectra ( $\lambda_{\max}$ ) of such compounds are determined in different solvents for different derivatives. In this

**TABLE 1: Wavelength of the Maxima of the Absorption Spectra ( $\lambda_{\max}$ , nm) and the Deviation ( $\Delta\lambda$ , nm) for Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (PFC-2) Calculated at Different Theory Levels with and without Solvent (Heptane) Compared to the Experimental Data (in Hexane)**

PFC-2	closed		open A		open B	
	$\lambda_{\max}$	$\Delta\lambda$	$\lambda_{\max}$	$\Delta\lambda$	$\lambda_{\max}$	$\Delta\lambda$
experiment	575		280		280	
TD-BMK/6-31G**/EXP	540	35	267	13	263	17
TD-BMK/6-31G**/PCM//EXP	555	20	271	9	266	14
TD-B3LYP/MIDI//EXP	575	0	274	6	278	2
TD-B3LYP/MIDI//PCM//EXP	590	-15	284	-4	280	0
TD-B3LYP/6-31G**/EXP	586	-11	291	-11	286	-6
TD-B3LYP/6-31G**/PCM//EXP	603	-28	294	-14	289	-9
TD-M05-2X/6-31G**/PCM//EXP	549	16	265	15	260	20
TD-M05/6-31G**/PCM//EXP	607	-32	289	-9	284	-4

contribution, we predict the maxima of the absorption spectra ( $\lambda_{\max}$ ), taking into account the solvent effects, for both closed and open ring isomers and compare them with the benchmark set of experimental data. In order to make accurate predictions of the spectral properties, we ensure that the molecular geometry is in agreement with the experimental X-ray crystal structures, available for some of the diarylethene derivatives. We validate the ability of different DFT methods to predict the ground-state geometry for the open and closed isomers as well as that for some byproducts. Our goal is to establish a computational protocol to investigate structure–property relationships for the diarylethene derivatives, to guide the design of new photochromics.

## 2. Computational Details

All calculations were performed using the Gaussian 2003 package. Different levels of theory were used to find the best method for geometry optimization, followed by absorption spectra predictions. In order to validate the methods for accurate geometry prediction, complete optimization was performed for a benchmark set of diarylethene photochromic compounds (Figure 2a–d). We then compared the theoretical geometries to the X-ray determined ones.

The optimized structures were further used to predict the optical absorption spectrum of each molecule with the TD-DFT formalism. Of several excited states predicted by TD-DFT, only the one with the maximum oscillator strength was used for comparison with the experimental spectra. Often, this state was not the lowest excited state. Several exchange–correlation functionals were tested to select the best method to determine the absorption spectra for both isomeric forms of the different substituted diarylethenes.

The polarizable continuum model used in this study was the nonequilibrium solvation self-consistent reaction field theory as implemented in Gaussian 2003 (keyword SCRF=IEFPCM) with default empirical parameters, including atomic and solvent radii and fast  $\epsilon_{\infty}$  and slow  $\epsilon_0$  dielectric constants. The solvents modeled were those used in the benchmark experiments: benzene (Bz), dichloromethane (DCM), acetonitrile (ACN), and heptane (Hep), the last in place of hexane.

## 3. Results and Discussions

Table 1 reports the predicted absorption maxima of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (PFC-2) at the experimental X-ray geometry obtained with different TD-DFT exchange–correlation functionals (BMK, B3LYP, M05-2X, and M05) and basis sets (MIDI! and 6-31G\*\*).

**TABLE 2: Bond Length Alternation (BLA, Å) and Wavelength of the Maxima on the Absorption Spectra ( $\lambda_{\text{max}}$ , nm) for Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (PFC-2) and 1,2-Bis(2,5-dimethyl-3-thienyl)maleicanhydride (MA-hit) Calculated at Different Theory Levels and Compared to the Experimental Data (Solvent for PFC-2—Heptane and for Ma-hit—Benzene)<sup>a</sup>**

PFC-2	closed				open			
	BLA1	BLA2	$\lambda_{\text{max}}$	$\Delta\lambda$	BLA1	BLA2	$\lambda_{\text{max}}$	$\Delta\lambda$
experiment	0.085	0.055	575		−0.112	0.050	276	
TD-B3LYP/MIDI//AM1	0.103	0.085	605	−30	−0.093	0.052	269	7
TD-B3LYP/ MIDI//HF/STO-3G	0.147	0.141	514	61	−0.173	0.116	274	2
TD-B3LYP/MIDI//B3LYP/ MIDI!	0.089	0.056	588	−13	−0.096	0.067	290	−14
TD-B3LYP/MIDI//PCM/B3LYP/MIDI!	0.089	0.056	605	−30	−0.096	0.067	296	−20
TD-B3LYP/MIDI//PCM/PBE0/MIDI!	0.089	0.056	605	−30	−0.092	0.061	296	−20
TD-B3LYP/MIDI//PCM/B1B95/MIDI!	0.092	0.059	599	−24	−0.095	0.060	298	−22
TD-B3LYP/MIDI//BMK/MIDI!	0.110	0.080	564	11	−0.117	0.082	289	−13
TD-B3LYP/MIDI//PCM/BHandHLYP/MIDI!	0.107	0.075	572	3	−0.106	0.073	289	−13
TD-B3LYP/MIDI//HF/MIDI!	0.134	0.102	525	50	−0.129	0.058	272	4
TD-B3LYP/6-31G*/BMK/6-31+G*	0.098	0.072	573	2	−0.116	0.072	276	0
TD-B3LYP/6-31G*/BMK/6-311G*	0.100	0.076	558	17	−0.121	0.074	272	4
TD-B3LYP/6-31G*/B3LYP/6-31G*	0.082	0.057	602	−27	−0.111	0.065	283	−7
TD-B3LYP/MIDI//PCM/BMK/6-31G*	0.098	0.074	590	−15	−0.116	0.074	298	−22
TD-B3LYP/6-31G*/PCM/BMK/6-31G*	0.100	0.074	590	−15	−0.117	0.073	299	−23
TD-B3LYP/6-31G*/PCM/BMK/6-31G*/PCM	0.083	0.057	620	−45	−0.110	0.066	298	−22
TD-BMK/6-31G*/PCM/BMK/6-31G*/PCM	0.083	0.057	566	9	−0.110	0.066	274	2
TD-B3LYP/6-31G*/PCM/B3LYP/6-31G*/PCM	0.085	0.058	615	−40	−0.100	0.079	302	−26
TD-B3LYP/6-31G*/PCM/M05-2X/6-31G*/PCM	0.100	0.076	581	−6	−0.114	0.068	292	−16
TD-M05-2X/6-31G*/PCM/M05-2X/6-31G*/PCM	0.100	0.076	521	54	−0.114	0.068	262	14
TD-M05/6-31G*/PCM/M05-2X/6-31G*/PCM	0.100	0.076	585	−10	−0.114	0.068	287	−11

MA-hit	closed				open			
	BLA1	BLA2	$\lambda_{\text{max}}$	$\Delta\lambda$	BLA1	BLA2	$\lambda_{\text{max}}$	$\Delta\lambda$
experiment			510		−0.109	0.082	403	
TD-BMK/6-31G*/PCM/BMK/6-31G*/PCM	0.092	0.078	477	33	−0.101	0.087	383	20
TD-B3LYP/6-31G*/PCM/BMK/6-31G*	0.092	0.080	519	−9	−0.113	0.087	446	−43
TD-B3LYP/6-31G*/PCM/M05-2X/6-31G*/PCM	0.091	0.077	519	−9	−0.102	0.071	447	−44
TD-M05/6-31G*/PCM/M05-2X/6-31G*/PCM	0.091	0.077	520	−10	−0.102	0.071	423	−20

<sup>a</sup> See Figure 2a for a definition of BLA1 and BLA2.

It is evident from Table 1 that in order to accurately predict  $\lambda_{\text{max}}$ , implicit solvent is essential. Even though B3LYP/MIDI//PCM and B3LYP/6-31G\*/PCM performed slightly better for the closed ring isomers, M05/6-31G\*/PCM was selected as it reproduced  $\lambda_{\text{max}}$  for both open and closed isomers consistently.

Next, we conducted geometry optimization of PFC-2 with various exchange–correlation functionals, including B3LYP, BLYP, BHandHLYP, PBE0, TPSS, BMK, M05, and M05-2x, as well as other theoretical methods (AM1 and HF) using two basis sets (MIDI! and 6-31G\*) for both BLA and spectral maxima of PFC-2 as shown in Table 2. In addition to the detailed study of PFC-2, we also investigated a representative of a different class of diarylethenes, 1,2-bis(2,5-dimethyl-3-thienyl)maleicanhydride (MA-hit). This is the only maleic anhydride derivative with available X-ray data (open isomer only).<sup>31</sup> As shown in Table 2, TD-BMK/6-31G\*/PCM/BMK/6-31G\*/PCM predictions, which were in good agreement with experiment in the case of PFC-2, were not so accurate in the case of Ma-hit. The only method with good agreement for both BLA and absorption spectra prediction for both PFC-2 and MA-hit was found to be TD-M05/6-31G\*/PCM/M05-2X/6-31G\*/PCM.

The results presented in Tables 1 and 2 show that the methods that predict the BLA accurately do not give accurate spectral predictions. This is most likely a consequence of the implied adiabatic approximation to TD-DFT. In rigorous theory, frequency-dependent exchange–correlation kernels are required.<sup>32–34</sup> In practice, however, one may simplify this frequency dependence to a step function and use one exchange–correlation

**TABLE 3: Bond Length Alternation (BLA, Å) and Wavelength of the Maxima on the Absorption Spectra ( $\lambda_{\text{max}}$ , nm) for a Subset of Diarylethenes Calculated at the TD-M05/6-31G\*/PCM/M05-2X/6-31G\*/PCM Theory Level and Compared to Experimental Data**

	closed isomer			open isomer		
	BLA1	BLA2	$\lambda_{\text{max}}$	BLA1	BLA2	$\lambda_{\text{max}}$
PFC-1-d						
experiment <sup>a</sup>	0.095	0.091	505	−0.112	0.089	303
theory	0.106	0.087	505	−0.113	0.080	316
PFC-1-e						
experiment <sup>b</sup>			529	−0.132	0.095	
theory	0.113	0.093	526	−0.117	0.089	279
PFC-2						
experiment <sup>c</sup>	0.085	0.055	575	−0.112	0.050	276
theory	0.100	0.076	585	−0.114	0.068	287
PFC-2-et						
experiment <sup>d</sup>	0.089	0.059	600	−0.115	0.068	286
theory	0.101	0.075	611	−0.116	0.067	284
PFC-B						
experiment <sup>e</sup>	0.113	0.055	469	−0.120	0.053	274
theory	0.119	0.045	476	−0.102	0.057	251
PFC-5						
experiment <sup>f</sup>			632	−0.133	0.062	320
theory	0.101	0.071	611	−0.116	0.060	332
MA-hit						
experiment <sup>g</sup>			510	−0.109	0.082	403
theory	0.091	0.077	520	−0.102	0.071	423
rmsd	0.011	0.014	11	0.011	0.009	15

<sup>a</sup> Reference 35. <sup>b</sup> Reference 36. <sup>c</sup> Reference 37. <sup>d</sup> Reference 38.<sup>e</sup> Reference 39. <sup>f</sup> Reference 40. <sup>g</sup> Reference 31.



**TABLE 4: Maximum Absorption Wavelengths ( $\lambda_{\text{max}}$ , nm) Measured Experimentally and Predicted at Two Theory Levels, TD-B3LYP/6-31G\*/PCM (T1) and TD-M05/6-31G\*/PCM (T2)<sup>a</sup>**

molecule	solvent	closed					open				
		$\lambda$			$\Delta\lambda$		$\lambda$			$\Delta\lambda$	
		exp	T1	T2	T1	T2	exp	T1	T2	T1	T2
DCN-1 <sup>b</sup>	Bz	547	552	531	−5	16	412	457	433	−45	−21
DCN-2 <sup>b</sup>	Bz	574	556	533	18	41	390	480	377	−90	13
MA-1 <sup>c</sup>	Bz	560	525	531	35	29	335	397	380	−62	−45
MA-1-A <sup>d</sup>	Bz	544	538	531	6	13	417	504	475	−87	−58
MA-2 <sup>b</sup>	Bz	595	563	545	32	50	450	507	481	−57	−31
MA-2-A <sup>e</sup>	Bz	680	683	644	−3	36	—	498	493	—	—
MA-2-B <sup>e</sup>	Bz	628	624	598	4	30	—	504	481	—	—
MA-3 <sup>f</sup>	Bz	620	595	565	25	55	470	540	508	−70	−38
Mi <sup>g</sup>	Bz	512	496	500	16	12	370	391	374	−21	−4
MA-hit <sup>h</sup>	Bz	510	519	520	−9	−10	403	446	423	−43	−20
PFC-1 <sup>i</sup>	Hep	432	428	436	4	−4	316	342	332	−26	−16
PFC-1-a <sup>j</sup>	Hep	425	421	425	4	0	336	357	345	−21	−9
PFC-1-b <sup>j</sup>	Hep	469	462	466	7	3	312	311	322	1	−10
PFC-1-c <sup>k</sup>	Hep	534	522	528	12	6	234	288	280	−54	−46
PFC-1-d <sup>j</sup>	Hep	505	499	505	6	0	303	326	316	−23	−13
PFC-1-e <sup>j</sup>	Hep	529	517	505	12	24	—	285	266	—	—
PFC-2 <sup>m</sup>	Hep	575	590	585	−15	−10	280	298	287	−18	−7
PFC-2-a <sup>k</sup>	Hep	562	576	575	−14	−13	262	294	280	−32	−18
PFC-2-b <sup>k</sup>	Hep	597	602	593	−5	4	305	324	308	−19	−3
PFC-2-et <sup>n</sup>	Hep	600	613	611	−13	−11	286	303	288	−17	−2
PFC-3 <sup>o</sup>	CAN	605	610	604	−5	1	312	315	304	−3	8
PFC-4 <sup>o</sup>	CAN	612	619	610	−7	2	320	321	312	−1	8
PFC-5 <sup>p</sup>	DCM	632	629	611	3	21	320	356	332	−36	−12
PFC-6 <sup>q</sup>	CAN	565	552	534	13	31	340	368	356	−28	−16
PFC-6-A <sup>e</sup>	Hep	665	653	625	12	40	—	375	355	—	—
PFC-7 <sup>q</sup>	CAN	612	596	585	16	27	290	334	327	−44	−37
PFC-8 <sup>r</sup>	Hep	517	523	521	−6	−4	258	269	261	−11	−3
PFC-9 <sup>s</sup>	Bz	828	787	792	41	36	354	379	358	−25	−4
PFC-B <sup>i</sup>	Hep	469	491	476	−22	−7	274	258	251	16	23
rmsd					16	24				42	24

<sup>a</sup> Both use geometry optimized at the M05-2X/6-31G\*/PCM level for open and closed isomers of diarylethenes in solution. Deviations of the theoretical values from the experimental ones ( $\Delta\lambda_{\text{max}}$ , nm) are also reported. <sup>b</sup> Reference 9. <sup>c</sup> Reference 8. <sup>d</sup> Reference 41. <sup>e</sup> Reference 7. <sup>f</sup> Reference 42. <sup>g</sup> Reference 43. <sup>h</sup> Reference 31. <sup>i</sup> Reference 44. <sup>j</sup> Reference 45. <sup>k</sup> Reference 46. <sup>l</sup> Reference 36. <sup>m</sup> Reference 37. <sup>n</sup> Reference 38. <sup>o</sup> Reference 47. <sup>p</sup> Reference 40. <sup>q</sup> Reference 48. <sup>r</sup> Reference 49. <sup>s</sup> Reference 6. <sup>t</sup> Reference 39.

functional to describe the ground state while using another frequency-independent functional to describe all of the low-lying excited states. After a number of functionals were considered, the ones with a higher (42–56%) fraction of HF exchange (BMK and M05-2X) were found to better predict the ground-state geometry, while the functionals with the lower (~20–30%) fraction of HF exchange predicted the excitation energies more accurately, when combined with linear response adiabatic TD-DFT. Finally, we selected the combination TD-M05/6-31G\*/PCM/M05-2X/6-31G\*/PCM to be giving the most accurate predictions consistently for both BLA and  $\lambda_{\text{max}}$  values for the molecules considered.

Furthermore, for a subset of diarylethenes with reported X-ray structures, we predicted both the BLA and the maxima in the absorption spectra using an implicit solvent model for both closed and open isomers (Table 3) at the TD-M05/6-31G\*/PCM/M05-2X/6-31G\*/PCM level.

For the rest of the molecules in the benchmark set, single crystal X-ray diffraction data were not available. We report their maximum absorption wavelengths at two theory levels, TD-M05/6-31G\*/PCM and TD-B3LYP/6-31G\*/PCM (with the geometry optimized at the M05-2X/6-31G\*/PCM level) and compare our predictions with the experimental  $\lambda_{\text{max}}$  values in Table 4. From Table 4, one can see that the average deviation in the maximum wavelengths obtained with the M05 functional is 24 nm for both open and closed forms, and the maximum signed errors are 55 (closed) and −58 nm (open), while for

B3LYP, the average deviations are 42 (open) and 16 nm (closed), and the maximum signed errors are 41 (closed) and −90 nm (open). The overall error predicted with the B3LYP functional is only slightly higher than that for M05 functional. However, the B3LYP error is more than twice larger for the open than that for the closed isomer. Apparently, B3LYP overestimates the degree of conjugation across the twisted torsion angles in the open form. Thus, we elected to use the M05 functional since it produces acceptable  $\lambda$  values for both of the isomers and gives consistent agreement with experiment for all subclasses of diarylethenes considered in this work: maleic anhydrides, perfluorocyclopentenes, and dicyanodiarlethenes.

The photochromic effect involves photochemical pericyclic reactions proceeding on the excited-state potential surfaces and thermal cycloreversion reactions following the ground-state potential energy surface. Thus, both the relative energies and the transition states of the conformers need to be described equally well. Only a few exchange–correlation functionals were designed to give accurate energies for both transition-state and equilibrium geometries. They accomplished this by combining an increased fraction of Hartree–Fock exchange with the dependence on the kinetic energy density. Among them are Boese–Martin functional for kinetics (BMK)<sup>50</sup> and Minnesota functional 2005 with double exact exchange (M05-2X), developed by Zhao and Truhlar.<sup>51</sup> While organic reaction barriers were deliberately excluded from the training set used in

parametrization of BMK, the M05-2X functional was designed with organic reactions in mind and was shown to perform better than other functionals for a wide range of organic reactions and molecular properties.<sup>52,53</sup> As a part of an ongoing investigation, we found that M05-2X also results in improved predictions of excited-state potential surfaces.<sup>54</sup> For these reasons, we used M05 and M05-2X functionals in our study.

#### 4. Conclusions

Several exchange–correlation functionals in combination with the TD-DFT formalism were evaluated for predictions of the absorption spectra for both closed and open isomers of diarylethene photochromic compounds. Bond length alternation descriptors were employed to select a suitable exchange–correlation functional to predict the equilibrium geometry in these compounds. We found that (a) the most accurate equilibrium geometry based on BLA parameters is calculated at the M05-2x/6-31G\*/PCM level, (b) the spectral data is best reproduced at the TD-M05/6-31G\*/PCM level with the root-mean-square deviation from the observed values in the range of 25 nm, (c) use of polarization basis set functions is important to obtain the best geometry, and (d) solvent effects as described by the polarizable continuum model (PCM) are important for accurate predictions of spectral data with TD-DFT. We recommend the TD-M05/6-31G\*/PCM/M05-2X/6-31G\*/PCM theory level for prediction of the structural and spectral parameters (BLA and  $\lambda_{\text{max}}$  values) for both closed and open isomers of diarylethene derivatives.

We have shown that an accurate molecular structure and an account of solvent effects are important for predictions of the optical properties in this class of molecules. We intend to use the established protocol in computational design of new photochromic materials. However, in order to describe other properties and functions of the photochromic compounds, one has to go beyond the equilibrium geometry and stationary properties. Our study of thermochemical kinetics of the cycloreversion and molecular mechanisms of photofatigue is presently under way. Its results will be published elsewhere.

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