

A Computational Comparative Study for the Spectroscopic Evaluation of Triazine Derivative Dyes in Implicit Solvation Model Systems Using Semi-Empirical and Time-Dependent Density Functional Theory Approaches

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The spectroscopic data for a range of cyclopenta-[*d*][1,2,3]-triazine derivative dyes have been evaluated using various standard computational approaches. Absorption data of these dyes were obtained using the ZINDO/S semi-empirical model for vertical excitation energies of structures optimised with the AM1, PM3, and PM6 methods. These studies were conducted under vacuum and solution states using the polarisation continuum model (PCM) for implicit solvation in the linear response model. The accuracy, along with the modest computational costs of using the ZINDO/S prediction, combined with the PM3 optimisation method for absorption data was reliable. While a higher computational cost is required for the time-dependent density functional theory (TDDFT), this method offers a reliable method for calculating both the absorption and emission data for the dyes studied (using vertical and adiabatic excitation energies, respectively) via state-specific solvation. This research demonstrates the potential of computational approaches utilising solvation in evaluating the spectroscopic properties of dyes in the rational design of fluorescent probes.

Keywords: spectroscopic evaluation, PM3, ZINDO, TDDFT, computational chemistry, implicit solvation, rational chemical design, computational chemical design, computational cost.

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Introduction

Computational methods utilised in the chemical sciences present versatile modelling tools for predicting the properties and performance of molecules under vacuum, in the solution state, and even in simulated biological systems. The spectroscopic properties of fluorescent dyes, namely cyclopenta-[*d*][1,2,3]-triazine derivatives have been investigated by other researchers.^[1–3] Here, we evaluate several computational methods for predicting the spectroscopic properties of this class of triazine dye.

The computational methods used to evaluate the spectroscopic transitions in implicit solvation systems include the wavelengths of electronic transitions for ground-state absorption, excited-state emission, and the oscillator strength (*f*). The *f*-value is a dimensionless quantity that measures the probability of electronic excitations occurring between molecular orbitals.^[4] This value can be correlated with the experimental absorption and emission intensity. In addition, electronic transitions between molecular orbitals, such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap, can be modelled.

The semi-empirical methods for ground state structure optimisation based on the Neglect of Diatomic Differential Overlap (NDDO) approach^[5] were selected based on their relatively low computational cost, including the Austin Model 1 (AM1),^[6] parametric method 3 (PM3),^[7,8] and parametric method 6 (PM6)^[9] approaches. These optimisation models were paired with Zerner's Intermediate Neglect of Differential Overlap (ZINDO)^[10] to model absorption data through single-point energy (SPE) calculations in the first excited state, notably, without optimisation of the excited state geometry (i.e. vertical excitation energy). Thus, the SPE calculations are expected to provide reasonably accurate spectroscopic data for the third-row element heteroatoms with 3d orbitals attached to the triazine skeleton.

The semi-empirical approaches reported for other fluorescent dyes have been reported to yield acceptably accurate spectroscopic data.^[11–17] Nevertheless, the presence of the sulfur atom in proximity with a N-heterocyclic ring structure was considered to significantly destabilise the ring due to the inductive effect, which may provide a difficult system to model

computationally, especially if the sulfur atom causes geometric perturbation^[16] and inaccurate spectroscopic data estimation as reported in Tubert-Brohman et al.^[18] As a result of these complexities, the lower computational cost of the semi-empirical methods compared with *ab initio* methods had to be weighed against the accuracy of the spectroscopic data acquired. Nevertheless, absorbance data of a satisfactory accuracy has been obtained for conjugated ring structures containing sulfur substituents using semi-empirical optimisation methods combined with the ZINDO/S model.^[12,13]

Despite the higher computational cost involved in using time-dependent density functional theory (TDDFT) methods, it is increasingly becoming the preferred computational approach for spectroscopic evaluation,^[19] including for studies of triazine derivative dyes.^[20] It has been established that the TDDFT approach has rendered semi-empirical methods such as ZINDO/1 almost obsolete for predicting the emission data of fluorescent dye molecules, involving optimisation of the excited-state structure (i.e. adiabatic excitation energy).^[19]

Therefore, this study investigates semi-empirical methods for evaluating the absorbance data of triazine derivative fluorescent dyes both under vacuum and in solution, using the linear response method^[21] combined with the polarisation continuum model (PCM) to model solvation. In addition, we compare the accuracy of TDDFT for predicting both absorption and emission data for this class of triazine dye. Also, we compare the basic linear response model and the more accurate state-specific solvation approach^[22] – accounting for the non-equilibrium solvation of the excited-state structure. It is expected that the application of computational cost across different synthetic designs could assist chemists to predict spectroscopic properties of dyes with geometric perturbation defects before synthesis.

Experimental

The synthesis and characterisation of compounds **1** to **7** have previously been reported.^[1–3] The absorption and emission measurements of compounds **1** to **3** of the original sample were measured directly without further purification, and compounds **4** to **7** were obtained from the literature.^[3] RCI Labscan supplied all the HPLC grade solvents used for the absorption and emission measurements for compounds **1** to **3**, except for dimethyl formamide (DMF) and acetonitrile (MeCN) which were dried over molecular sieves (4 Å pellets, with 1.6 mm diameter). The steady-state absorption and emission measurements of compounds **1–3** were recorded at room temperature using Cary 50 BIO UV/Vis and Fluorolog 22 (Jobin Yvon Horiba) spectrophotometers.

The structures were produced and visualised using *Avogadro* (software version 1.90.0).^[23] Calculations were completed using *Gaussian 16* software (Wallingford, Connecticut, USA) (full reference provided in the Supplementary Material) for all methods utilised. The triazine derivative dyes **1** to **7** were initially subject to geometry optimisation through the Berny analytical gradient method^[24] incorporated into *Gaussian 16* followed by vibrational frequency analysis. All structures were confirmed to be stable intermediates (minima on the potential energy surface) and ensured no imaginary frequencies present during simulation. Solvation of dyes **1** to **7** was modelled through the self-consistent reaction field (SCRF) approach^[25] with the PCM.^[26] The following solvents: dimethyl sulfoxide (DMSO), MeCN, tetrahydrofuran (THF), toluene, and DMF were implemented by specifying them from the built-in solvent

list contained in *Gaussian 16* software. The 2-methyltetrahydrofuran (2-MeTHF) was implemented by specifying the specific solvent characteristics from the literature values (see Supplementary Material).

For the semi-empirical approaches, the structures were optimised using either the AM1, PM3, or PM6 method followed by SPE calculations at the ZINDO/S semi-empirical level, specified by 10 singlet excited states. For the TDDFT analysis, the ω B97X-D long-range corrected hybrid exchange-correlation functional^[27] was selected mainly for its ability to model long range interactions and proven performance in TDDFT studies.^[28] In addition, when combined with the 6–31G(d) basis set,^[29,30] it provided suitably accurate data for a reasonable computational cost. Therefore, for this study, six singlet excited states were specified for TDDFT analysis. The linear response and state-specific solvation approaches were utilised for calculating absorption data using TDDFT while the state-specific approach was utilised for excited state emission data.

Results and Discussion

The wavelength of the maximum absorption ($\lambda_{\text{grd}}^{\text{calc}}$) and the corresponding f values for triazine derivative dyes **1** to **7** determined using the semi-empirical methods trialled in this investigation are provided in Table 1. Ten excited states were specified to gain a solid understanding of the electronic transitions occurring. The vertical excitation energies are provided in Table 2. In all cases, the absorption wavelength ($\lambda_{\text{grd}}^{\text{calc}}$) recorded in Table 1 corresponded to the first strongly allowed electronic transition – that is, the first electronic transition to possess an oscillator strength (f) value greater than 0.08.^[28,31] The maximum absorption wavelengths obtained experimentally are also provided.

The AM1 semi-empirical method combined with ZINDO/S consistently predicted $\lambda_{\text{grd}}^{\text{calc}}$ values greater than the values recorded experimentally for triazine dyes **1** to **7** in each solvent (obtained either from Zhu et al.^[3] or measured directly). As previously reported by other investigators, the AM1 method is less parameterised than either the PM3 or PM6 semi-empirical methods.^[7–9,32] This may explain some of the issues observed in accurately modelling the relatively complex triazine dye structures investigated in this study. Moreover, the sulfur atom bonded to the heterocyclic nitrogen ring present in each triazine derivative dye **1** to **7** may inhibit the ability of the AM1 method to accurately optimise the structures.

The combined PM3 semi-empirical method with ZINDO/S provided data with relatively close agreement to experimentally observed absorption data. This combination of methods provided an impressive correlation between the experimental and calculated absorption maxima. Triazine derivative dye **4** (MOT) was modelled accurately for the combined PM3 with ZINDO/S. Several studies have also reported the increased tendency of the PM3 geometry optimisation method to provide more accurate starting structures for calculation of absorption data compared with the AM1 method.^[7,8,32]

The implicit solvation of dyes through the linear response method proved relatively effective for PM3 combined with ZINDO/S, proving capable of reproducing the experimental solvatochromic trends. Solvents recording higher bathochromic shifts (i.e. DMSO) generally recorded the longer wavelengths in the ground state, $\lambda_{\text{grd}}^{\text{calc}}$, while shorter wavelengths were recorded for THF and 2-MeTHF (which recorded close values). MeCN demonstrated variable changes in absorption maxima for both the experimentally recorded and computationally observed data.

Table 1. Spectroscopic data obtained from semi-empirical methods and experimental values

Ground state absorption maxima ($\lambda_{\text{grd}}^{\text{calc}}$) and oscillator strength (f) of triazine dyes **1** to **7** calculated using ZINDO/S for vertical excitation energies. Experimental data were either obtained from ref. [3] or measured directly. ND, not determined

Dye	Medium	$\lambda_{\text{grd}}^{\text{exp}}$	AM1		PM3		PM6	
			$\lambda_{\text{grd}}^{\text{calc}}$	f	$\lambda_{\text{grd}}^{\text{calc}}$	f	$\lambda_{\text{grd}}^{\text{calc}}$	f
BPT 1	Vacuum	ND	401	0.265	374	0.090	388	0.243
	DMSO	385	420	0.277	386	0.169	412	0.309
	THF	381	418	0.279	385	0.180	409	0.288
	MeCN	380	420	0.239	391	0.144	410	0.301
	2-MeTHF	381	420	0.259	385 ^A	0.180 ^A	411	0.260
	Toluene	385	416	0.282	386	0.192	408	0.199
MPT 2	Vacuum	ND	401	0.249	374	0.080	387	0.229
	DMSO	387	429	0.315	384 ^A	0.167 ^A	411	0.291
	THF	384	418	0.259	394	0.177	408	0.271
	MeCN	389	419	0.254	382	0.162	410	0.284
	2-MeTHF	384	418	0.259	394	0.177	408	0.270
	Toluene	387	422	0.280	392	0.170	407	0.224
BDT 3	Vacuum	ND	400 ^A	0.257 ^A	376	0.128	389	0.251
	DMSO	382	422 ^A	0.270 ^A	387	0.169	413	0.327
	THF	379	420	0.285	384	0.176	411	0.314
	MeCN	378	420 ^A	0.267 ^A	386	0.166	411	0.307
	2-MeTHF	378	420	0.285	384	0.177	411 ^A	0.313 ^A
	Toluene	384	420	0.301	385	0.195	410	0.245
MOT 4	Vacuum	ND	389	0.272	364	0.150	373	0.213
	DMSO	388	420	0.324	387	0.181	402	0.244
	THF	381	416	0.320	383 ^A	0.168 ^A	399	0.271
	MeCN	381	417	0.319	386	0.178	401	0.240
	DMF	389	420	0.325	387	0.183	402	0.245
AMT 5	Vacuum	ND	395	0.257	373	0.103	383	0.253
	DMSO	401	423 ^A	0.312 ^A	394	0.168	410 ^A	0.301 ^A
	THF	393	419	0.307	386	0.154	406	0.304
	MeCN	393	420	0.307	393	0.163	408 ^A	0.295 ^A
	DMF	404	423	0.313	394	0.167	411 ^A	0.302 ^A
BMT 6	Vacuum	ND	395	0.220	375	0.082	383	0.175
	DMSO	406	424	0.264	395	0.167	410	0.234
	THF	397	421	0.262	391	0.169	410	0.223
	MeCN	396	423	0.260	394	0.164	408	0.228
	DMF	409	424	0.265	395	0.168	410	0.234
EOT 7	Vacuum	ND	397	0.254	379	0.130	387	0.263
	DMSO	399	419	0.260	385	0.167	407	0.288
	THF	393	417	0.268	384	0.182	408	0.307
	MeCN	395	417	0.256	384	0.164	405	0.283
	DMF	397	419	0.261	386	0.169	407	0.289

^AStructure optimised based on negligible forces.

One plausible explanation could have been that the MeCN formed a complex triad group, making it difficult to model the triazine dye structures accurately for implicit solvent that involved MeCN for **1** to **7**. The PM3 method predicted relatively accurate absorption maxima for triazine derivative dyes **1** to **4** and reflected greater absorbance values for **5** (AMT) and **6** (BMT) (although less accurate for these dyes). However, the PM3 method was unsuccessful at reproducing the high absorption values for dye **7** (EOT) in the various solvents, indicating that this method is not universally accurate. Apparently, the combined methods of PM3 with ZINDO/S provides a valuable tool for synthetic chemists aiming to rapidly predict the spectroscopic properties of newly functionalised triazine derivative dyes before synthesis.

The combined PM6 semi-empirical method with ZINDO/S calculated absorption data did not agree with the experimentally observed data. Each calculation predicted relatively higher values than the experimentally observed absorption maxima.

While the PM6 semi-empirical method is relatively new and more parameterised than the PM3 method,^[9] the extra parameterisation was not successful at predicting the complex structure of the triazine dyes **1** to **7**, making PM3 the most accurate semi-empirical method for geometry optimisation trialled in this study.

It was also observed that the AM1, PM3, and PM6 methods required almost the same computational costs to complete calculations. Triazine derivative dye **1** (BPT) consistently required the greatest computational costs in each solvent trialled at the AM1, PM3, and PM6 levels. This is potentially due to the structural positioning of the benzyl group attached to a sulfide bond and the pyrrolidine group (Fig. 1). In comparison, triazine derivative dyes **5** (AMT) and **7** (EOT) recorded the lowest computational costs, which may likely be due to the simplicity of their structures (Fig. 1). For triazine derivative dyes **1** (BPT), **2** (BDT), and **3** (MPT), the greatest computational costs were recorded for calculations specifying 2-MeTHF as the solvent, as

Table 2. Vertical excitation energies (ΔE) for triazine dyes **1** to **7** calculated using ZINDO/S with the AM1, PM3, and PM6 semi-empirical optimisation methods

Dye	Medium	AM1		PM3		PM6	
		ΔE [eV]	$\Delta E (\times 10^{-4})$ [cm ⁻¹]	ΔE [eV]	$\Delta E (\times 10^{-4})$ [cm ⁻¹]	ΔE [eV]	$\Delta E (\times 10^{-4})$ [cm ⁻¹]
BPT 1	Vacuum	3.0918	3.8332	3.3153	4.1103	3.1985	3.9655
	DMSO	2.9489	3.6561	3.2116	3.9818	3.0113	3.7334
	THF	2.9684	3.6803	3.2215	3.9941	3.0302	3.7569
	MeCN	2.9493	3.6566	3.1730	3.9339	3.0241	3.7493
	2-MeTHF	2.9538	3.6622	3.2229 ^A	3.9958 ^A	3.0176	3.7413
MPT 2	Toluene	2.9780	3.6922	3.2125	3.9829	3.0387	3.7674
	Vacuum	3.0935	3.8354	3.3118	4.1060	3.2034	3.9716
	DMSO	2.8928	3.5865	3.2340 ^A	4.0096 ^A	3.0150	3.7380
	THF	2.9676	3.6793	3.1489	3.9040	3.0360	3.7641
	MeCN	2.9576	3.6669	3.2424	4.0200	3.0277	3.7538
BDT 3	2-MeTHF	2.9687	3.6806	3.1497	3.9050	3.0367	3.7649
	Toluene	2.9380	3.6426	3.1611	3.9192	3.0437	3.7736
	Vacuum	3.0979 ^A	3.8408 ^A	3.2992	4.0904	3.1893	3.9541
	DMSO	2.9391 ^A	3.6439 ^A	3.2071	3.9762	2.9989	3.7181
	THF	2.9520	3.6599	3.2249	3.9983	3.0147	3.7377
MOT 4	MeCN	2.9518	3.6597	3.2152	3.9862	3.0189	3.7429
	2-MeTHF	2.9529	3.6610	3.2248	3.9981	3.0156 ^A	3.7388 ^A
	Toluene	2.9489	3.6561	3.2171	3.9886	3.0277	3.7538
	Vacuum	3.1860	3.9500	3.4097	4.2274	3.3197	4.1158
	DMSO	2.9539	3.6623	3.2038	3.9721	3.0809	3.8197
AMT 5	THF	2.9836	3.6991	3.2364 ^A	4.0125 ^A	3.1044	3.8489
	MeCN	2.9702	3.6825	3.2144	3.9853	3.0948	3.8370
	DMF	2.9529	3.6610	3.2032	3.9714	3.0811	3.8200
	Vacuum	3.1352	3.8871	3.3243	4.1215	3.2405	4.0176
	DMSO	2.9345 ^A	3.6382 ^A	3.1478	3.9027	3.0209 ^A	3.7453 ^A
BMT 6	THF	2.9566	3.6656	3.2079	3.9772	3.0548	3.7874
	MeCN	2.9506	3.6582	3.1609	3.9189	3.0362 ^A	3.7643 ^A
	DMF	2.9330	3.6364	3.1496	3.9049	3.0197 ^A	3.7439 ^A
	Vacuum	3.1381	3.8907	3.3083	4.1017	3.2363	4.0124
	DMSO	2.9217	3.6224	3.1410	3.8942	3.0267	3.7525
EOT 7	THF	2.9438	3.6498	3.1705	3.9308	3.0276	3.7537
	MeCN	2.9339	3.6375	3.1506	3.9062	3.0374	3.7658
	DMF	2.9210	3.6215	3.1414	3.8947	3.0261	3.7518
	Vacuum	3.1233	3.8723	3.2745	4.0598	3.2034	3.9716
	DMSO	2.9573	3.6665	3.2178	3.9895	3.0494	3.7807
	THF	2.9748	3.6882	3.2262	3.9999	3.0378	3.7663
	MeCN	2.9703	3.6826	3.2284	4.0026	3.0612	3.7953
	DMF	2.9560	3.6649	3.2162	3.9875	3.0470	3.7777

^AStructure optimised based on negligible forces.

the 2-MeTHF is not included in the list of built-in solvents within *Gaussian 16* software. Therefore, it had to be manually specified for each computation study.

The presence of a sulfur atom on the triazine dye was replaced with an oxygen atom to form dye **8** (ETC) (see Fig. 2). Absorbance data for dye **8** (ETC) was obtained using the ZINDO/S method applied to structures optimised with the AM1, PM3, and PM6 methods indicated in Table 3. The vertical excitation energies (ΔE) are recorded in Table 4. Interestingly, the semi-empirical methods trialled for dye **8** (ETC) gave values close to the recorded values for dye **7** (EOT). Thus, the PM3 optimisation method provided structures for ZINDO/S calculations that predicted considerably lower λ_{grd}^{calc} values than the AM1 or PM6 optimisation method; regardless of the substitution of the sulfur atom. Therefore, it is probable that the lower accuracy recorded for the semi-empirical methods was not solely due to the presence of the sulfur atom but influenced by additional structural factors, for instance, the triazine ring.

While the semi-empirical methods are sufficient at calculating vertical excitation energies for providing ground-state absorption data, improved emission data was obtained using the TDDFT method. TDDFT allowed for adiabatic excitation energy calculation through excited-state geometry optimisation. Furthermore, TDDFT offers a higher accuracy for the spectroscopic prediction of the triazine dyes **1** to **7** compared with the semi-empirical methods but with a greater computational cost.^[33] Accordingly, utilising TDDFT accurately predicted the ground state absorption (λ_{grd}^{calc}), the excited state emission (λ_{exc}^{calc}), and the *f*-value of triazine derivative dye **7** (EOT) at the ω B97X-D/6–31G(d) level, as indicated in Table 5. The vertical and adiabatic excitation energies are recorded in Table 6. These values corresponded to the experimental absorption and emission data (λ_{grd}^{exp} and λ_{exc}^{exp} , respectively). The data was calculated under vacuum and solvated in DMSO and THF using the PCM model. The absorption data was calculated using the linear response and state-specific solvation models while emission data was calculated using only the state-specific approach.

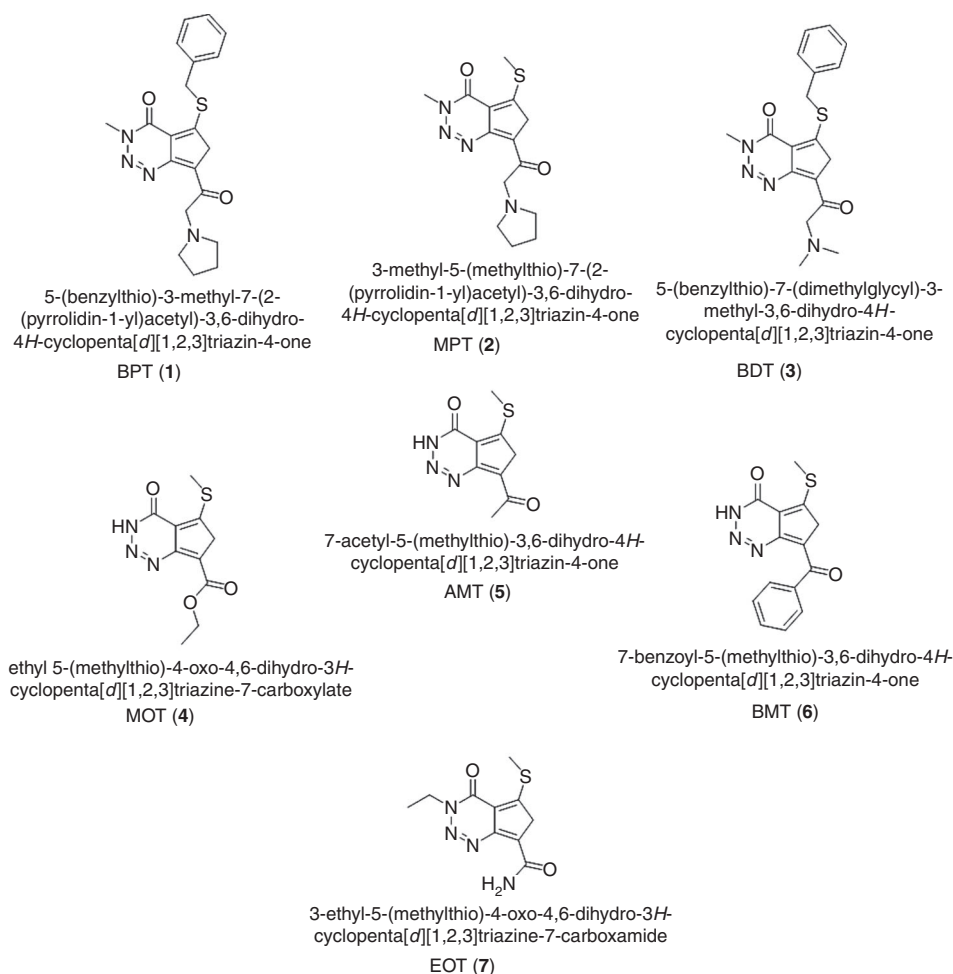


Fig. 1. The structure, IUPAC nomenclature, and abbreviated names of the triazine dyes **1** to **7** studied here.

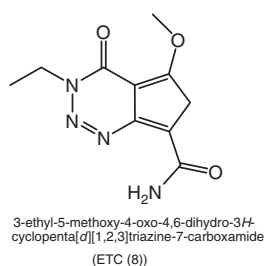


Fig. 2. The structure, IUPAC nomenclature, and abbreviated name of the model triazine dye, 3-ethyl-5-methoxy-4-oxo-4,6-dihydro-3*H*-cyclopenta[*d*][1,2,3]triazine-7-carboxamide (**8**, ETC).

The effect of solvation was calculated to decrease the HOMO–LUMO energy gap, indicated by the increase in both the maximum absorption and emission wavelengths for solvation in DMSO and THF relative to the calculation completed under vacuum. An analogous bathochromic shift was observed for each of the semi-empirical calculations in each solvent relative to the value recorded under vacuum. Analysis of the electronic transition data for dye **7** (EOT) calculated through TDDFT also demonstrated that both the absorbance and emission maxima were due to the same electronic transition involving the HOMO and LUMO molecular orbitals (with a relative contribution > 97 % in all cases). Fig. 3 demonstrates the shapes of the HOMO – 1, HOMO, LUMO, and LUMO + 1

molecular orbitals for dye **7** (EOT) calculated through TDDFT. It can be observed that each of the molecular orbitals possess a considerable electron density on the conjugated ring structures, contributing to the absorption and emission properties observed. The effect of altering the electron withdrawing substituents attached to the rings will decrease the electron density present on the ring structures, thus altering the energy levels of molecular orbitals and changing the spectroscopic properties observed.

Both the linear response solvation model and the state-specific approach provided absorption data (via directly computed vertical excitation energies) that corresponded relatively closely to the experimental data. Furthermore, the emission data calculated through the state-specific approach produced data that corresponded to the experimental data. Thus, the computational data in this study demonstrates that TDDFT analysis may be suited for the accurate predictions of emission data of this class of fluorescent dyes as well. Nonetheless, TDDFT analysis required by far the greatest computational cost techniques investigated in this work. This computational cost is expected to increase even more for more complex structures, such as triazine dye **1** (BPT). Nevertheless, the increased computational cost is necessary for estimating accurate emission data that can satisfactorily model experimental spectra.

An additional set of vertical excitation energy calculations were conducted for dye **7** (EOT) using the ZINDO/S semi-empirical method on structures optimised at the ω B97X-D/6–31G(d) level.

Table 3. Spectroscopic data obtained by semi-empirical methods for a model triazine dye, ETC (8)

Ground state absorption maxima ($\lambda_{\text{grd}}^{\text{calc}}$) and oscillator strength (f) calculated using ZINDO/S for vertical excitation energies with the AM1, PM3, and PM6 semi-empirical optimisation methods

Medium	AM1		PM3		PM6	
	$\lambda_{\text{grd}}^{\text{calc}}$	f	$\lambda_{\text{grd}}^{\text{calc}}$	f	$\lambda_{\text{grd}}^{\text{calc}}$	f
Vacuum	390	0.270	381	0.206	391	0.264
DMSO	414	0.262	402	0.171	420 ^A	0.279 ^A
THF	411	0.278	400	0.222	417	0.291
MeCN	412	0.258	401	0.170	418	0.277
DMF	414	0.264	402	0.173	420	0.283

^AStructure optimised based on negligible forces.

Table 4. Vertical excitation energies (ΔE) calculated for ETC (8) calculated using ZINDO/S with the AM1, PM3, and PM6 semi-empirical optimisation methods

Medium	AM1		PM3		PM6	
	ΔE [eV]	$\Delta E (\times 10^{-4}) [\text{cm}^{-1}]$	ΔE [eV]	$\Delta E (\times 10^{-4}) [\text{cm}^{-1}]$	ΔE [eV]	$\Delta E (\times 10^{-4}) [\text{cm}^{-1}]$
Vacuum	3.1760	3.9376	3.2543	4.0347	3.1699 ^A	4.0347
DMSO	2.9968	3.7155	3.0847	3.8244	2.9519	3.8244 ^A
THF	3.0132	3.7358	3.0980	3.8409	2.9723	3.8409
MeCN	3.0101	3.7320	3.0957	3.8381	2.9656	3.8381
DMF	2.9955	3.7139	3.0846	3.8243	2.9502	3.8243

^AStructure optimised based on negligible forces.

Table 5. Comparative electronic ground state absorption ($\lambda_{\text{grd}}^{\text{calc}}$) and excited state emission ($\lambda_{\text{exc}}^{\text{calc}}$) data with the corresponding oscillator strengths (f) for EOT (7)

Calculated using ZINDO/S applied to geometry optimised at the $\omega\text{B97X-D/6-31G(d)}$ level or using TDDFT analysis. Experimental data were either obtained from ref. [3] or measured directly. $\lambda_{\text{grd}}^{\text{exp}}$ and $\lambda_{\text{exc}}^{\text{exp}}$ are the experimental absorption and emission maxima respectively. Computational absorptions were calculated using (i) the linear response or (ii) state-specific solvation models. The emission data were calculated only through the state-specific approach. ND, not determined

Calculation	Medium	$\lambda_{\text{grd}}^{\text{exp}}$ [nm]	$\lambda_{\text{grd}}^{\text{calc}}$ [nm]	f
ZINDO/S, obtained from vertical excitation energies, linear response solvation	Vacuum ^A	ND	397	0.279
	DMSO	399	418	0.325
	THF	393	416	0.323
TDDFT, obtained from vertical excitation energies, linear response solvation	Vacuum ^A	ND	396	0.166
	DMSO	399	405	0.213
	THF	393	405	0.211
TDDFT, obtained from vertical excitation energies, state-specific solvation	DMSO	399	401	0.168
	THF	393	401	0.167
		$\lambda_{\text{exc}}^{\text{exp}}$ [nm]	$\lambda_{\text{exc}}^{\text{calc}}$ [nm]	
TDDFT, obtained from adiabatic excitation energies, state-specific solvation	Vacuum ^A	ND	501	0.125
	DMSO	527	517	0.125
	THF	496	514	0.125

^ACalculations completed under vacuum involve no implicit solvation model.

Calculations were carried out using the linear response solvation model in an analogous method to that applied to structures optimised using the AM1, PM3, and PM6 semi-empirical methods (see Tables 5 and 6). Interestingly, absorbance data predicted by ZINDO/S for structures optimised at the $\omega\text{B97X-D/6-31G(d)}$ level were considerably higher than the experimental

absorbance maxima and relatively close to the data yielded for ZINDO/S calculations applied to structures optimised at the AM1 and PM6 levels. Therefore, the experimental data of the ZINDO/S method combined with the PM3 optimisation method may be due to a cancellation of errors between the optimised structures and the subsequent ZINDO/S vertical excitation

Table 6. Vertical and adiabatic excitation energies for triazine dye, EOT (7)

ΔE calculated using ZINDO/S applied to geometry optimised at the ω B97X-D/6–31G(d) level and using TDDFT analysis. Experimental data were either obtained from ref. [3] or measured directly. Absorption data was calculated using both the linear response and the state-specific solvation models. The emission data was calculated using only the state-specific approach

Calculation	Medium	ΔE [eV]	$\Delta E (\times 10^4)$ [cm ⁻¹]
ZINDO/S, obtained from vertical excitation energies, linear response solvation	Vacuum ^A	3.1247	3.8740
	DMSO	2.9674	3.6790
	THF	2.9790	3.6934
TDDFT, obtained from vertical excitation energies, linear response solvation	Vacuum ^A	3.1280	3.8781
	DMSO	3.0591	3.7927
	THF	3.0589	3.7925
TDDFT, obtained from vertical excitation energies, state-specific solvation	DMSO	3.0929	3.8346
	THF	3.0922	3.8337
TDDFT, obtained from adiabatic excitation energies, state-specific solvation	Vacuum ^A	2.4738	3.0670
	DMSO	2.4003	2.9759
	THF	2.4134	2.9922

^ACalculations completed under vacuum involve no implicit solvation model.

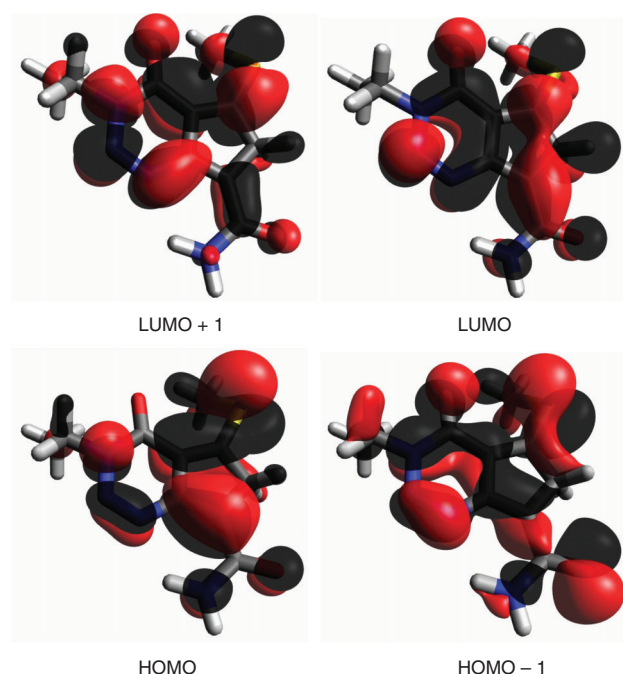


Fig. 3. Visualisation of the HOMO – 1, HOMO, LUMO, and LUMO + 1 molecular orbitals for dye 7 (EOT) in DMSO calculated at the ω B97X-D/6–31G(d) level (structures visualised using *Avogadro* software version 1.2.0).

calculations. Nevertheless, the combination of the PM3 optimisation method with ZINDO/S may prove useful, especially for providing a rapid method for predicting the spectroscopic properties for this class of dyes.

Conclusion

Computational approaches were used to model the spectroscopic data of a class of triazine derivative dye through the implicit solvation model. From the three semi-empirical methods (AM1, PM3, and PM6) utilised for geometry optimisation in conjunction with the ZINDO/S for calculating vertical excitation energies, the PM3 model produced the most promising method. For PM3 combined with ZINDO/S, absorbance data with a reasonably low computational cost was obtained. However, it should be considered that the closer agreement of the combination of PM3 with ZINDO/S may be due to a cancellation of errors between the two

methods. In addition, TDDFT analysis completed at the ω B97X-D/6–31G(d) level was used to predict absorption and emission data through both the linear response and the state-specific approach. The calculated data corresponded to the experimental data but the considerable computational cost limits the accessibility of this investigation to 7 (EOT) only in this study. We expect this method to be applicable to other classes of dyes as well.

Supplementary Material

The full reference details for *Gaussian 16* software and the solvent parameters utilised to model 2-methyltetrahydrofuran (2-MeTHF) are available on the Journal's website.

Data Availability Statement

All data are either presented in this manuscript or are available from the corresponding author on request.

Conflicts of Interest

The authors declare no conflicts of interest.

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