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REGULAR ARTICLE

A quantitative prediction of the electronic spectra of thiocarbonyl chromophores: TD-DFT versus SAC-CI

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Abstract In this contribution, we set up a SAC-CI methodology to evaluate the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ vertical transition energies of a series of thiocarbonyl derivatives. We show that Frozen-Core SAC-CI provides accurate vertical excitations energies. Nevertheless, in order to obtain converged results, the R2S2 unliked integrals have to be taken into account in L3-SAC-CI calculations. In addition, we present the comparative performances of three computational procedures, INDO/S, TD-DFT, and SAC-CI, for the calculation of valence excited states energies and it turns out that: (1) no tuning of the *exact exchange* (α) included in TD-DFT allows to consistently reproduce the SAC-CI results; (2) SAC-CI and TD-B3LYP both evaluate the $n \rightarrow \pi^*$, as well as the $\pi \rightarrow \pi^*$ transition energies, with a similar accuracy.

Keywords SAC-CI · TD-DFT · Thiocarbonyl · Dyes · Absorption spectra

1 Introduction

Various theoretical models can be applied to predict the colour of dyes. Based on empirical considerations, a basic approach takes advantage of first-order additive group contributions to foresee the auxochromic effects on $\lambda_{\max}$. Such rules are of practical interest [1,2] but they often lack transferability, and are limited by the available experimental input. To overcome this difficulty, one could go for semi-empirical methods to model hypothetical structure. Nevertheless, these approaches suffer unpredictable accuracies for $\lambda_{\max}$ [3,4]. A third strategy, that relies on ab initio calculations for the evaluation and prediction of UV/Vis spectra of molecules, is the time dependent density functional theory (TD-DFT) which often gives accurate results [5–15].

Of course TD-DFT does not include all electron correlation effects. A major, though costly, improvement can be obtained with the coupled cluster (CC) theory that more accurately and consistently treats the dynamic electron correlation. For a correct calculation of the low-lying and the Rydberg states energies, one can trust the symmetry-adapted cluster-configuration interaction method (SAC-CI), [16–19] that is closely related to the CC method. Several applications of the SAC-CI model recently appeared in the literature. For instance, Yokojima et al. studied the absorption spectra of the open/closed neutral/cationic forms of diarylethene photochroms by using SAC-CI/6-31G[6-31G(d) for S atom] and TD-B3LYP/6-31G(d) levels of approximation [20]. The maximal absorption wavelengths of the open/closed neutral diarylethene are provided within a precision varying from 0.04/0.19 eV for SAC-CI to 0.25/0.09 eV for TD-B3LYP. Concerning the open/closed cationic forms, SAC-CI calculations yield MAE (mean average error) of 0.19/0.01 eV, whereas the TD-B3LYP deviations are of 0.10/0.22 eV. Saha et al. have calculated the $\lambda_{\max}$ of poly(*para*-phenylene vinylene) using SAC-CI/6-31G(d) with an average MAE of 0.17 eV, [21] while with the aug-cc-PVTZ basis set, Li et al. calculated the valence (Rydberg) $\pi \rightarrow \pi^*$ transition of benzene with typical errors of 0.13 (0.18) eV with SAC-CI, and 0.20 (0.25) eV with TD-B3LYP. They also calculated the $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ vertical energies of pyrimidine (pyrazine) with SAC-CI (SD-R) MAE of 0.12/0.32 eV (0.05/0.62 eV), respectively [22].

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Table 1 Comparison between the gas-phase SAC-CI(FC,R2S2,L3)/6-311+G(2df,p)//B3LYP/6-311G(2df,p), TD-B3LYP/6-311+G(2df,p)//B3LYP/6-311G(2df,p), and INDO/S//AM1 approaches used for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies

	SAC-CI		TD-B3LYP		INDO/S	
Compounds	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
–diNH$_2$	4.36	5.23 (*0.248*)	4.09	5.08 (*0.103*)	3.15	4.51 (*0.247*)
–NH$_2$,Me	3.32	4.97 (*0.269*)	3.31	5.10 (*0.176*)	2.75	5.01 (*0.345*)
–diMe	2.35	6.19 (*0.165*)	2.52	5.53 (*0.186*)	2.34	5.53 (*0.354*)
–Me,Cl	2.52	5.36 (*0.108*)	2.69	5.85 (*0.180*)	2.40	5.41 (*0.363*)
–diH	2.37	6.80 (*0.265*)	2.22	6.31 (*0.204*)	2.15	6.10 (*0.393*)
–diCl	2.81	5.49 (*0.237*)	2.74	4.94 (*0.111*)	2.74	5.39 (*0.375*)
–diF	3.70	6.38 (*0.226*)	3.63	6.15 (*0.150*)	2.74	5.39 (*0.375*)
–Cl,F	3.20	5.84 (*0.260*)	3.19	6.06 (*0.190*)	2.74	5.39 (*0.375*)

The excitation energies are given in eV. For the records, the associated oscillator strengths f are provided in italics

In this work, we firstly set up a SAC-CI based methodology in order to evaluate the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ vertical transition energies of a series of eight target thiocarbonyl derivatives for which experimental $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies are available [23]. Secondly, we compare the accuracy of two other theoretical approaches INDO/S, TD-DFT, with SAC-CI performances for the evaluation of UV/Vis spectra. The active transition in thiocarbonyls (in the visible) has a $n \rightarrow \pi^*$ nature, for which the absorption coefficient remains strong enough to make these dyes effective [24–26], the first dipole-allowed transition ($\pi \rightarrow \pi^*$) showing up in the UV region. According to Griffiths [24], thiocarbonyl derivatives constitute the most important class of $n \rightarrow \pi^*$ dyes. It also presents potential medicinal uses [27].

2 Methodology

All our calculations have been performed with the GAUSSIAN 03 suite of programs [28]. A three-step methodology was considered: (1) the optimisation of the ground-state structure, (2) the calculation of the Hessian; and (3) the evaluation of the electronic excited-states. The SCF convergence criteria was set to 10^{-9} a.u., whereas the ground-state structures were optimised until the residual mean force was smaller than 1.0×10^{-5} a.u. For the semi-empirical INDO/S, AM1 structures were selected, while for the ab initio schemes, the geometry optimisations were performed with B3LYP [29]/6-311G(2df,p) that has been shown to yield accurate and converged geometries, i.e. the 6-311G(2df,p) geometry is quasi-identical to geometries optimized with a larger basis set for thiocarbonyl dyes [30]. The calculated B3LYP geometries are provided in Supplementary Materials for the 8 structures of Table 1.

For each molecule, the excited-state energies were computed with INDO/S, TD-DFT and SAC-CI, the two latter using the extended 6-311+G(2df,p), known to provide perfectly converged wavelengths for the first absorption peak in thiocarbonyls [23]. For INDO/S, only the fluorine atom has been parametrized for the halogen series in Ref. [28], so that the chlorine derivatives have been treated using the F parameters. This constitutes one of the semi-empirical model practical drawbacks that we wish to underline. Note that we used the Zerner's spectroscopic parameters for INDO/S implemented in the GAUSSIAN 03 version [28].

The environmental effects were evaluated by means of the Polarizable Continuum Model (IEF-PCM), [31] that represents the solvent as a structure-less material, characterised by its macroscopic properties. We selected the so-called non-equilibrium procedure for TD-DFT calculations, that has been designed for the study of absorption processes. [32] The solvents used are cyclohexane (CH), heptane (Hpt), and diethylether (DEE), which are found in the solvent list available for the PCM implementation in GAUSSIAN 03. Nevertheless, as the diethylether EPSINF (relative dielectric constant at infinite frequency, ϵ_∞) value is missing in the current Gaussian implementation, we have used 1.82 [33].

3 Results

3.1 Methodological set up for the SAC-CI calculations

In the first step, we have assessed the parameters required for meaningfull SAC-CI calculations. This aspect might look quite technical, though to our best knowledge it has not been recently treated in details. The target molecule was the di-fluoro-thiocarbonyl, and the starting procedure was SAC-CI/6-311G+(2df,p)//B3LYP/6-311G(2df,p). The notation "//" separate the level of theory used for excited state calculations (on left) and the one used for ground state geometry optimisation (on right): the excited states energies are evaluated at the SAC-CI framework using the 6-311+G(2df,p) basis set, whereas the ground state geometry is optimized with B3LYP/6-311G(2df,p) approach. In the SAC-CI framework, one can tune the threshold for the double excitation operators from Level 3 (the most accurate) to Level 1 (the fastest). Using L1 instead of L3 induces a decrease of the excitation energies from 3.64 eV to 3.51 eV for the $n \rightarrow \pi^*$ transition and from 6.34 eV to 6.15 eV for $\pi \rightarrow \pi^*$. Heading to the intermediate Level 2 only slightly reduces the gap with the L3 benchmark: we calculate transition energies of 3.56 eV for $n \rightarrow \pi^*$ and 6.23 eV for $\pi \rightarrow \pi^*$. Since the discrepancies between L1 or L2, on the one side, and L3 on the other side remain large, we select the most accurate L3 for the SAC-CI calculations.

Freezing the core electrons during the calculation (FC option) tunes the results by a small amount for both excitations, 3.70 eV for $n \rightarrow \pi^*$ and 6.38 eV for $\pi \rightarrow \pi^*$, that is 0.05 eV off the full option results. However, if one ignores the R2S2 unlinked integrals (we neglect the quadruple excitations used in the SD-R formalism for the singlet excited states description), the differences between frozen and full results are much larger, 0.27 eV for the $n \rightarrow \pi^*$ and 0.23 eV for $\pi \rightarrow \pi^*$; one cannot discard these unliked terms. As a compromise between decreased accuracy and computational requirements, we opted out for the SAC-CI(FC,R2S2,L3) level of theory. Nevertheless, our investigations suggest that getting converged transitions energies with SAC-CI could be a difficult task, as these energies are very sensitive to the selected parameters. For the ground-state geometries, B3LYP structures provide $\lambda_{\max}$ very close to those computed with CCSD(T) geometries. Indeed, at the SAC-CI//CCSD(T) level of approximation, we get for the di-fluoro-thiocarbonyl a $\lambda_{\max-1}$ ($\lambda_{\max-2}$) value of 3.70 eV (6.37 eV).

3.2 Comparison between SAC-CI, TD-B3LYP, and INDO/S results

A comparison between the gas-phase INDO/S, TD-B3LYP, and SAC-CI $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies for the –diNH$_2$, –NH$_2$,Me, –diMe, –Me,Cl, –diH, –diCl, –diF, and the –Cl,F derivatives (the structures are shown in the Fig. 1) is shown in Table 1. For the first valence excited-state ($n \rightarrow \pi^*$), Table 1 indicates that the agreement between results from TD-DFT and SAC-CI is satisfactory, with an averaged absolute deviation limited to 0.12 eV. However, for the $\pi \rightarrow \pi^*$ excited-state the differences between the two ab initio methods are much larger, 0.37 eV in average. In addition, only three molecules, –Me,Cl, –NH$_2$,Me, and –Cl,F, show greater TD-B3LYP excitation energies values than their SAC-CI counterparts. For the $n \rightarrow \pi^*$ transition, most of the TD-B3LYP results are below the corresponding SAC-CI values. Consistently with recent investigations, [21, 22] we conclude that TD-B3LYP transition energies are often underestimated as long as SAC-CI is chosen as a reference. In Ref. [22], Li et al. suggested that one of the origins of this quasi-systematic TD-B3LYP underestimation can be traced back to the deficiency in the long-range behaviour of the potential associated with the B3LYP functional. Table 1 also provides a comparison between INDO/S//AM1 and SAC-CI transition energies. There is no major surprise: the semi-empirical method only provides poor results. Indeed, the INDO/S//AM1 approach delivers low quality estimates for both the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. This is illustrated by the MAE (related to SAC-CI results) that amounts to 0.45 eV (0.46 eV) for the $n \rightarrow \pi^*$ ($\pi \rightarrow \pi^*$) transition. Compared to the TD-B3LYP results, the semi-empirical $n \rightarrow \pi^*$ MAE is four times larger, whereas the $\pi \rightarrow \pi^*$ MAE is even worse by ~ 0.10 eV. Moreover, INDO/S provides nearly always smaller $n \rightarrow \pi^*$ energies than the corresponding TD-DFT and SCA-CI data.

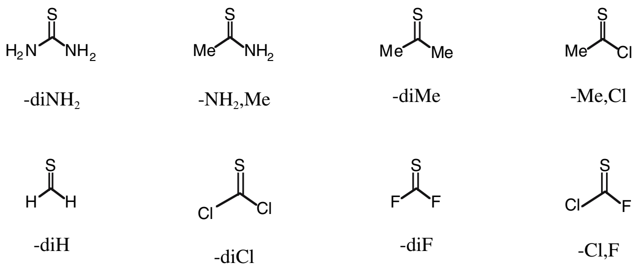

Fig. 1 Sketch of the eight studied thiocarbonyl derivatives

As previously suggested, [34] we performed a calibration of the *exact* exchange percentage α value included in B3LYP to assess the feasibility of reaching SAC-CI-like results. Note that several investigations evaluating the impact of modifying the *exact* HF exchange on the computed electronic excitation spectra can be found in the literature. For instance, Dierksen and Grimme performed a detailed (TD)-DFT study of the influence of α parameter on the vibronic structures of large molecule. They conclude that hybrid functionals with $\alpha = 30$–40% provide the smallest theory-experiment errors [35]. Moreover, in order to correctly describe the excited charge-transfer states, Dreuw and Head-Gordon designed new long-range hybrids [36].

The scan of the HF exchange contribution has been performed with successive α values going from 0.0 to 1.0 by a 0.1 step. A zero value for α corresponds to the pure BLYP functional, whereas a 1.0 value corresponds to a TD-HF calculation (we neglect the effects of the LYP correlation functional). The value of α was tuned for TD-DFT calculations while the ground-states geometries were B3LYP for each step. The tables that show the α-dependence of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ calculated in gas-phase are provided in Supplementary Material. The α values allowing the best results w.r.t. SAC-CI, are listed in Table 2. For the $n \rightarrow \pi^*$ transition, one can built up a first group for which the optimal

Table 2 List of the “best SAC-CI-like” α values

	optimal α	
Compounds	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
–diNH_2	0.388	0.329
–NH_2,Me	0.210	<0.0
–diMe	<0.0	>1.0
–Me,Cl	<0.0	<0.0
–diH	0.550	<0.0
–diCl	0.402	>1.0
–diF	0.328	>1.0
–Cl,F	0.233	=1.0

The values correspond to the gas-phase TD-B3LYP(α)/6-311+G(2df,p)//B3LYP/6-311G(2df,p) level of theory

factor is included in the [0.2–0.4] window: $\alpha = 0.233, 0.328, 0.402$, and 0.388 for –Cl,F, –diF, –diCl, and –diNH_2 derivatives. The second group is constituted by the -Me derivatives for which the optimal $\alpha \leq 0.2$. From a more general point of view, it is impossible to calibrate the α to SAC-CI $n \rightarrow \pi^*$, whatever the chemical class of the target dye. As an example, for the nitroso (Me–NO), the SAC-CI transition energy is calculated at 1.75 eV, whereas the TD-DFT results are of 1.86 eV for $\alpha = 0$ (BLYP) and 1.84 eV for $\alpha = 1.0$: there is no optimal value for this class.

For $\pi \rightarrow \pi^*$, three halogeno derivatives (–diCl, –diF, and –Cl,F) and the –diMe-thiocarbonyl constitute the first group with $\alpha \geq 1.0$ whereas the second group is made of the mixed –NH_2 and –Me,Cl derivatives as well as the thiocarbonyl for which the optimal scale factor is negative. For the rest of the set of molecules, we get a quite scattered distribution for α: 0.550 for the –diH $n \rightarrow \pi^*$, 0.329 for the $\pi \rightarrow \pi^*$ –diNH_2. Obviously, each compound has its proper optimal scale factor, and for the full set, it is consequently impossible to set a really optimal α value.

3.3 Comparison between SAC-CI, TD-B3LYP, INDO/S and experiment

In this section, we studied the UV/Vis spectra of thiocarbonyl derivatives in gas and solvent-phase. Therefore the excitation spectra have been calculated within the TD-DFT and SAC-CI frameworks without taking into account the relaxation effects. Indeed, the selected experiments provide vertical excitation energies (UV/Vis spectroscopy in gas and/or solvent-phase).

Table 3 provides the comparison between PCM-SAC-CI, PCM-TD-B3LYP, PCM-INDO/S, and the experimental values; it is also depicted in Figs. 2 and 3 for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. For the liquid-phase SAC-CI, it is currently impossible to directly combine PCM and SAC-CI calculations with the GAUSSIAN 03 suite of programs. Nevertheless, the solvent effects were approximated by means of an additive scheme: for example, for the –diNH_2 derivative, we calculated a solvatochromic shift of +0.29 eV for the $n \rightarrow \pi^*$ transition when going from gas-phase TD-B3LYP to PCM-TD-B3LYP/6-311+G(df,p)//PCM-B3LYP/6-311G(2df,p), whereas it amounts to +0.05 eV for the $\pi \rightarrow \pi^*$ transition (see Tables 1 and 3). Consequently, the gas-phase SAC-CI data were shifted by these amounts. Concerning the $\pi \rightarrow \pi^*$, we show that both SAC-CI and TD-DFT systematically overestimate the vertical energies by 0.56 and 0.49 eV, respectively. The INDO/S scheme provides an intermediate MAE of 0.52 eV. Ab initio methods provide more accurate values for the $n \rightarrow \pi^*$ transition with MAE of 0.20 and 0.093 eV for SAC-CI and TD-B3LYP, respectively, whereas INDO/S almost systematically underestimates the vertical energies by 0.38 eV, the MAE=0.38 eV and the MSE $= -0.32$ eV.

4 Conclusions

We firstly investigated the performances of the SAC-CI scheme for the calculation of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$

Table 3 Comparison between liquid-phase SAC-CI(FC,R2S2,L3)/6-311+G(2df,p)//B3LYP/6-311G(2df,p), TD-B3LYP/6-311+G(2df,p)//B3LYP/6-311G(2df,p), INDO/S//B3LYP/6-311G(2df,p) transition energies, and the experimental data

		SAC-CI		TD-B3LYP		INDO/S		Exp./Ref. [2]	
Compounds	Solvent	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
–diNH_2	DEE	4.65	5.28	4.38	5.13	3.58	4.69	4.28	4.90
–NH_2,Me	Hpt	3.43	4.92	3.42	5.05	2.95	4.72	3.38	4.64
–diMe	CH	2.38	–	2.55	–	2.49	–	2.48	–
–Me,Cl	CH	2.54	5.32	2.71	5.81	2.66	5.15	2.84	4.11
–diCl	CH	2.81	5.39	2.74	4.84	2.78	5.36	2.63	4.78
–diF	gas	3.70	6.38	3.63	6.15	2.74	5.38	3.52	6.08

All values are in eV
DEE diethylether, *Hpt* heptane, *CH* cyclohexane

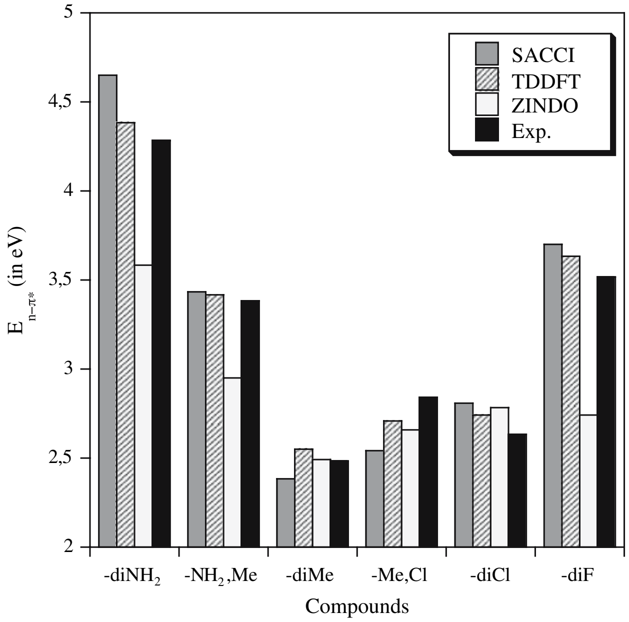

Fig. 2 Comparison between TD-B3LYP, SAC-CI, INDO/S, and the experimental excitation energies (in eV) for $n \rightarrow \pi^*$ transitions

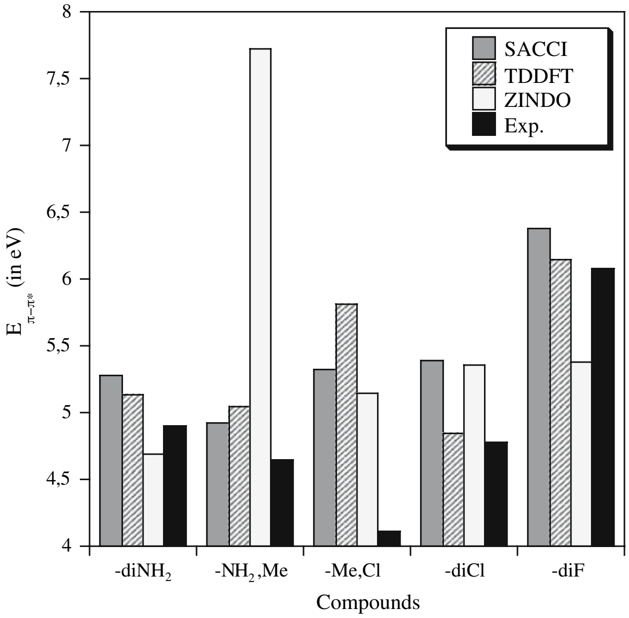

Fig. 3 Comparison between TD-B3LYP, SAC-CI, INDO/S, and the experimental excitation energies (in eV) for $\pi \rightarrow \pi^*$ transitions

transitions energies of thiocarbonyl dyes. Secondly, we compared the merits of INDO/S, TD-DFT, and SAC-CI for the calculation of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ for a set of eight thiocarbonyl derivatives. To ensure converged results, all calculations were carried out using the 6-311+G(2df,p) basis set for the excited-states, and the 6-311G(2df,p) for the ground-state.

Here, we have assessed the parameters required for meaningfull SAC-CI calculations and we have shown that frozen-core SAC-CI can be used for vertical excitations without significant loss of accuracy. Nevertheless, in order to obtain converged results, the R2S2 unliked integrals have to be taken into account in L3-SAC-CI calculations. Secondly, starting with B3LYP, the Hartree-Fock exchange (*exact* exchange α) percentage used was optimised to reach excitation energies that are similar to SAC-CI data. It turns out that no optimal α values can be simultaneously found for both transitions. Finally, we compared the INDO/S, the TD-B3LYP and the SAC-CI results with experimental data and we demonstrated that for the $\pi \rightarrow \pi^*$, neither the ab initio (even if TD-B3LYP and SAC-CI provide $\pi \rightarrow \pi^*$ energies with a similar accuracy estimated at 0.5 eV), nor the semi-empirical methods were able to accurately evaluate the excitation energies. TD-B3LYP (INDO/S) provides the most (less) accurate $n \rightarrow \pi^*$ energies with an absolute deviation of 0.093 eV/0.38 eV.

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