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Ab Initio Calculation of the Electronic Spectrum of Azobenzene Dyes and Its Impact on the Design of Optical Data Storage Materials

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Abstract: Electronic excitation energies of 16 azobenzene dyes have been calculated by ab initio methods within the second-order polarization propagator approximation (SOPPA). Good agreement with expriment is found for the lowest singlet and triplet states for both the *trans*- and *cis*-azobenzene molecules. The differences are in the range of ±0.3 eV, with the exception of the lowest $n \rightarrow \pi^*$ transition in *trans*-azobenzene, where a deviation of −0.64 eV is found. The lowest $\pi \rightarrow \pi^*$ transition in *trans*-azobenzene, on the other hand, is particularly well reprensented with a deviation of only −0.15 eV. Furthermore, the experimental singlet $\pi \rightarrow \pi^*$ transitions are reproduced for a set of azobenzene dyes with different electron donor and acceptor groups and the correct shifts in excitation energy are obtained for the different substituents. It has also been demonstrated that ab initio methods can be used to determine suitable candidates for azo components used in materials for data storage.

I. Introduction

The photophysical properties of azo compounds are of large interest in the development of nonlinear optical materials and materials for optical storage of data. In particuler, azobenzene dyes linked to side chains of different polymers and oligomers have been exploited extensively for holographic and digital storage of information in thin films of these materials.[1−11] The principle of the holographic storage process in azobenzene polymer films is that polarized light is used to excite the *trans* conformation of the azobenzene dyes which then isomerizes to the *cis* conformation. Since polarized light is used, the dyes with a transition dipole moment orthogonal to the external field are not excited. The *cis* conformation relaxes back to the *trans* conformation in a new arbitrary orientation. If the process is carried out repeatedly, the azobenzenes will be aligned. The diffraction is different for the part of the material where the dyes are aligned and this information is read by another laser. Fast optical recording in a permanent manner with high read-out efficiencies has been demonstrated. Total erasure of the inscribed information and multiple reuse of the material have also been achieved.

One crucial aspect of this process that can be studied by theoretical models is the required laser wavelength to obtain the *trans*-to-*cis* isomerization in an azobenzene dye. The isomerization is induced by an electronic excitation of an electron in either the highest occupied nonbonded orbital (denoted *n*) or in the highest occupied π orbital to the lowest unoccupied π orbital (denoted π^*). In *trans*-azobenzene (TAB), the lowest excited singlet state, S_1, is mainly due to the $n \rightarrow \pi^*$ transition whereas the S_2 state is mainly due to the $\pi \rightarrow \pi^*$ transition.[12] If we assume that the geometry of TAB is planar, the oscillator strength of the $n \rightarrow \pi^*$ transition is zero due to symmetry arguments, which means that it is small also for slightly nonplanar conformations. Thus, to excite the molecule a laser wavelength is often chosen to match the $\pi \rightarrow \pi^*$ transition. However, the isomerization process of azobenzene involves also the S_1 state as well as the lowest triplet states, T_1 and T_2.[12]

In some storage devices, it may be desirable to use lasers with long wavelengths. At red and infrared wavelengths, cheap

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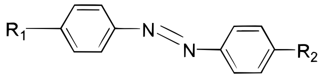
and compact semiconductor diode lasers are available. Lower excitation energies can be achieved either by adding electron donor and acceptor groups to azobenzene[13,14] or by replacing one of the phenyl rings with for example a thiazole unit.[15,16] Although a rather extensive number of experimental data are available,[14] it is difficult to get a systematic picture of how different combinations of functional groups at various positions on the azo dyes affect the excitation energies and thereby also to design a suitable diazo component for a storage device. For such a study, ab initio quantum chemical calculations would in principle be a fruitful tool since, ideally, only the geometry of the molecules has to be specified in an input to a "black-box" model. However, an accurate calculation of the electronic spectrum of a π-conjugated or aromatic molecule is a nontrivial task,[17−19] even if accurate calculations of stilbene, a similar molecule to the ones considered in this work, have been carried out.[20,21] Aspects such as the molecular geometry, basis set, as well as the inclusion of electron correlation, and then especially the multiconfigurational nature of both the ground state and the excited states have to be considered in detail.

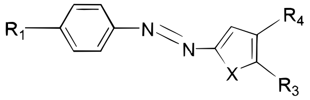
Previous theoretical investigations of the electronic structure of azobenzene dyes have been limited to semiempirical calculations apart from a few exceptions. Semiempirical calculations of their electronic excitation energies[22−33] and of its optical properties[27−31] have been carried out. Furthermore, density functional theory (DFT) and second-order Møller−Plesset (MP2) calculations have been used to calculate the structure and vibrational frequencies of azobenzene[34,35] and their excited states have been studied by a configuration interaction (CI) method,[36] but in this latter study the basis set was limited to the STO-3G basis set.

The purpose of this work is 2-fold. We would like to investigate if the approximations adopted in the model here are valid. We have therefore calculated the excitation energies to the lowest singlet and triplet states of *trans*-azobenzene (TAB) and *cis*-azobenzene (CAB). Furthermore the S_1 and S_2 excitation energies of substituted TAB (**1**) were calculated for different substitutents R_1 and R_2, for which experimental data are available. Second, we would like to investigate in more detail how different substituents affect the excitation energies and then especially how the excitation energies can be lowered. We have therefore included also oxazole and thiazole units (**2**) as well as a benzo[*b*]oxazole unit (**3**) in our investigation.

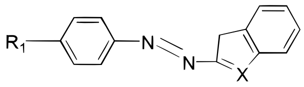
(1)



(2)



(3)



II. Calculational Aspects

The aim of this work is to use TAB (**1**) as a template molecule and calculate the excitation energies of the S_1 and S_2 states for different azo dyes. For the relatively large set of molecules included in this work, it is of importance to use a method that is more or less a "black box". For this reason, we have chosen to use the second-order polarization propagator approximation (SOPPA),[37−39] which is an extension of the random-phase approximation (RPA). In SOPPA the electronic excitation energies and oscillator strengths are evaluated through second order in Møller−Plesset perturbation theory.[37] The SOPPA method used in calculations of electronic excitation energies can thus be considered as an analogue to MP2 used for the calculation of vibrational frequencies. A restriction of SOPPA is that it is based on a single-determinant expansion of the wave function, but as is demonstrated in this work, both the S_1 and S_2 states are to a large extent due to single-electron excitations. Therefore, SOPPA should be expected to give good results for these excitations of the azobenzenes. For comparison, we have also included results for the doubles corrected RPA, RPA(D), method,[40] which was used also as a starting point for the direct SOPPA calculations.[39] It should be noted that the electronic excitation energies calculated in this work are vertical excitation energies, i.e. the energy difference between an excited and the ground electronic state at the same geometry. This is a theoretical quantity which, however, can be used as an approximation to the experimental absorption maxima.

In the SOPPA calculations of the singlet excitation energies, we have normally calculated three excitation energies for each symmetry of the molecule. The lowest excitation energy in each symmetry was converged to 10^{-6} au and the remaining two excitation energies to 10^{-4} au. Excitations out of the 1s orbitals have been neglected and the 1s orbitals were also kept doubly occupied in the MP2 wave function. This frozen core approximation has been shown to work well in a previous SOPPA study of the excitation energies of benzene,[39] for which the excitation energies were changed by less than 0.01 eV and the oscillator strengths by less than 0.01. The oscillator strengths have been calculated in both the length and velocity representations. For more calculational details we refer to ref 39. In the calculation of triplet excitation energies, we have used the traditional SOPPA implementa-

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Table 1. Bond Distances (Å) and Bond Angles (deg) Employed in This Work

trans-azobenzene[a]		oxazole		substituents	
$r(C_\phi-C_\phi)$	1.385	$r(C-O)$	1.36	$r(C_\phi-O_{sp})$	1.45
$r(C_\phi-H)$	1.084	$r(C-N)$	1.34	$r(C_{sp}-N)$	1.16
$r(C_\phi-N_{azo})$	1.437	$r(C-H)$	1.084	$r(C_\phi-O)$	1.36
$r(N_{azo}-N_{azo})$	1.257	$\angle(O-C-N_{azo})$	123.0	$r(O-H)$	0.96
$\angle(C_\phi-C_\phi-C_\phi)$	120	$\angle(N-C-N_{azo})$	123.0	$\angle(C_\phi-O-H)$	109.47
$\angle(C_\phi-C_\phi-H)$	120	$\angle(C-O-C)$	104.0	$r(C_\phi-C_{sp^3})$	1.43
$\angle(C_\phi-C_\phi-N_{azo})$	120	$\angle(C-N-C)$	104.0	$r(C_{sp^3}-H)$	1.09
$\angle(C_\phi-N_{azo}-N_{azo})$	113.0	$\angle(O-C-H)$	116.0	$\angle(O-C_{sp^3}-H)$	109.47
		$\angle(N-C-H)$	122.0	$r(C_\phi-C_{sp^3})$	1.52
cis-azobenzene				$r(C_\phi-N)$	1.40
$\angle(C_\phi-N_{azo}-N_{azo})$	121.9	thiazole		$r(N-H)$	1.01
$\angle(C_\phi-N_{azo}-N_{azo}-C_\phi)$	53.3	$r(C-S)$	1.72	$\angle(C_\phi-N-H)$	120
		$r(C-N)$	1.30	$r(C_\phi-Cl)$	1.70
		$r(C-H)$	1.084	$r(C_\phi-C_{sp^2})$	1.46
		$\angle(S-C-N_{azo})$	122.5	$r(C_{sp^2}-O)$	1.22
		$\angle(N-C-N_{azo})$	122.5	$r(C_{sp^2}-H)$	1.08
		$\angle(C-S-C)$	90.0	$\angle(C_\phi-C_{sp^2}-O)$	120
		$\angle(C-N-C)$	110.0	$\angle(C_\phi-C_{sp^2}-H)$	120
		$\angle(S-C-H)$	121.0	$r(C_{sp^2}-C_{sp^2})$	1.34
		$\angle(N-C-H)$	119.0	$\angle(C_{sp^2}-C_{sp^2}-H)$	120
		$\angle(C^b-N)$	1.34		

[a] C_ϕ denotes the carbon atoms in the ring systems. N_{azo} denotes the nitrogen atoms in the azo group. [b] The carbon not bonded to the azo group.

tion[38] of the 1.0 version of Dalton,[41] whereas for all singlet excitation energy calculations we have used a local version of the Dalton program,[41] which includes the atomic integral-direct SOPPA program[39,40] as well as the integral-direct coupled cluster program by Koch and co-workers.[42,43]

We have employed standard geometries for the azobenzene dyes, and thus no geometry optimizations have been carried out. TAB has been assumed to be planar and an experimental geometry has been adopted.[44] However, it is still controversial if TAB is planar or not and the planarity is probably sensitive to the surroundings of the molecule.[45,46,34] Nonetheless, the most accurate ab initio calculation results in a planar geometry for the isolated TAB molecule.[35] For CAB, we have used a nonplanar experimental geometry.[44] When different functional groups have been added to TAB, the same geometry has been used for azobenzene and standard geometries of the substituents have been taken from ref 47. For the oxazole and thiazole units, we have used geometries similar to the experimental geometries of the corresponding molecules (taken from refs 48 and 49), whereas we use the same geometries for the azo group and phenyl ring as for azobenzene. All the geometrical parameters are given in Table 1.

Table 2. Singlet Electronic Excitation Energies (eV) and Oscillator Strengths[a] of TAB[b]

state	type[c]	SOPPA/[3s2p1d/2s]	SOPPA/[3s2p(1d)/2s]	exptl[d]
1^1B_g	$n \to \pi^*$	2.31	2.49	2.95
1^1B_u	$\pi \to \pi^*$	3.71 (0.93/0.59)	3.90 (0.70/0.61)	3.86
2^1B_u	$\pi_2 \to \pi^*$	4.07 (0.03/0.02)	4.24 (0.02/0.02)	
2^1A_g	$\pi_3 \to \pi^*$	4.08	4.25	
3^1A_g	$\pi_4 \to \pi^*$	4.83	5.07	
2^1B_g	$n \to \pi_2^*$	5.50	6.07	
3^1B_u	$\pi \to \pi_2^*$	5.53 (0.37/0.27)	5.82 (0.25/0.27)	5.41
4^1A_g	$\pi \to \pi_3^*$	5.57	5.86	
1^1A_u	$\sigma \to \sigma^*$	5.58 (0.00/0.00)	6.13 (0.00/0.00)	
2^1A_u	$\sigma \to \sigma_2^*$	5.77 (0.00/0.00)	6.24 (0.00/0.00)	

[a] The oscillator strengths in velocity and length representation are given in parentheses. [b] Ground-state properties: E(MP2/ANO[3s2p1d/2s]) = −570.007119 au, E(MP2/ANO[3s2p(1d)/2s]) = −570.349067 au. [c] The dominant contribution to the excitation. [d] Reference 13.

Table 3. Triplet Electronic Excitation Energies (eV) of TAB]

state	SOPPA/[3s2p1d/2s]	SOPPA/[3s2p(1d)/2s]	exptl
1^3B_g	1.57	1.71	1.57[a]
1^3B_u	2.40	2.44	2.1[b]
1^3A_g	3.55	3.58	
2^3B_u	3.85	4.13	

[a] Reference 52. [b] References 53 and 52.

The basis sets considered here are the atomic natural orbital (ANO) basis sets by Widmark et al.[50,51] In the work by Molina et al. on the *trans*- and *cis*-stilbene molecules,[20,21] they used a [3s2p1d] contraction for carbon and a [2s] contraction for hydrogen which provided a good accuracy (this basis set is denoted [3s2p1d/2s]). We have also tested a smaller basis set where we only employ a [3s2p] contraction for carbon but a [3s2p1d] contraction for nitrogen. This basis set will be denoted [3s2p(1d)/2s] where [2s] is the contraction of the hydrogen basis. By inspection of the orbital coefficients, it may be implied that the two lowest singlet excitations are to a large extent localized to the azo group which may be justified by calculations. Results for the singlet and triplet states of TAB are presented in Tables 2 and 3, respectively, for both contractions of the basis set. In each entry of Table 2, the symmetry of the state and the dominant type of excitation with its amplitude in parentheses are presented. The length and velocity representations, respectively, of the oscillator strengths are given in parentheses with the corresponding excitation energy. It is found that the smaller basis set, [3s2p(1d)/2s], gives excitations in the same order and at most 0.25 eV higher than the [3s2p1d/2s] basis set for the lowest excitations. A similar basis set effect has been observed previously in SOPPA calculations of the excitation energies of naphthalene.[39] As expected, this is not true for the higher excitations since they mainly involve excitations in the phenyl rings and are then obviously more sensitive to the carbon basis. Since this investigation is limited to the two lowest

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Table 4. Electronic Excitation Energies (eV) and Oscillator Strengths[a] of CAB[b]

state	SOPPA/ [3s2p(1d)/2s]	exptl	state	SOPPA/ [3s2p(1d)/2s]	exptl
1^1B	2.52 (0.04/0.01)	2.8[c]	1^3B	1.57	1.26[d]
2^1B	4.30 (0.04/0.03)	4.4[c]	2^3B	3.29	
2^1A	4.51 (0.02/0.02)		1^3A	3.49	
3^1B	4.66 (0.12/0.09)		3^3B	4.19	

[a] The oscillator strengths in velocity and length representation are given in parentheses. [b] Ground-state properties: *E*(MP2/ANO[3s2p(1d)/2s]) = −570.334687 au. [c] Reference 22. [d] Reference 52.

singlet excitations, we have therefore chosen to adopt the [3s2p(1d)/2s] basis set in the main part of the calculations.

III. Results

A. The Electronic Spectrum of *trans*-Azobenzene. The calculated singlet excitation energies of TAB are given in Table 2. Experimentally, three bands are found around 2.95, 3.86, and 5.41 eV, respectively.[13] The band at 2.95 eV is assigned to the $n \rightarrow \pi^*$ transition,[13] which is approximately 0.6 eV higher than our most accurate value of 2.31 eV. It is noted that only nonplanar conformations of TAB give an oscillator strength for this excitation and our calculations are carried out for a planar geometry. It is, however, not necessary that the experimental *average* geometry is nonplanar, since the observed band can be due to molecular out-of-plane distortions that may have large oscillator strengths[12].

The second band at 3.86 eV has been identified as the $\pi \rightarrow \pi^*$ transition[13] and is in good agreement with our most accurate value of 3.71 eV. The difference in the calculated excitation energies for the two basis sets and the difference in oscillator strengths in the length and velocity representations indicate that larger basis sets may give significant contributions. The third band at 5.41 eV has been assigned to a combination of different excitations[13] and we also find several excitations around 5.5 eV.

Turning to the triplet states of TAB in Table 3, we also find good agreement with triplet quenching experiments.[52] The $n \rightarrow \pi^*$ transition is found at approximately 1.5 eV, in excellent agreement with our calculated value of 1.57 eV. Furthermore, we calculate the $\pi \rightarrow \pi^*$ transition to be 2.40 eV, which is in reasonable agreement with the conjectured experimental value of 2.1 eV.[53,52]

B. The Electronic Spectrum of *cis*-Azobenzene. The calculation of the singlet and triplet excitation energies of CAB (Table 4) has been restricted to the [3s2p(1d)/2s] basis set and therefore we present only the lowest excited states. First of all it is noted that the ground state of CAB is located 0.39 eV above the ground state of TAB at the MP2/[3s2p(1d)/2s] level of approximations. Experimentally, a singlet band is found at 2.8 eV with a low intensity,[22] in good agreement with our calculated value of 2.52 eV. The next experimental band is found at 4.4 eV, also with a low intensity,[22] and in our calculations we find several singlet excitations in this region. For the triplet excitations, the lowest state is found experimentally at 1.26 eV,[52] also in good agreement with our calculated value of 1.57 eV. In contrast to the TAB molecule, many types of excitations give contributions to each excited state and it is therefore more difficult to assign a type of excitation to each state of CAB as was done for TAB.

C. Singlet States of *trans*-Azobenzene Dyes. We have calculated the lowest singlet excitation energies for a set of 16 molecules. Two different sets have been studied. One set is based on the 4-substituted (and 4,4′-substituted) azobenzenes **(1)**, where experimental data exist for the $\pi \rightarrow \pi^*$ transitions for the molecules considered here (see ref 14 and references therein). This set was chosen to investigate whether the approximations adopted in this work, such as the choice of basis set and the use of standard geometries, give results close to experimental data and whether the same trends as compared to experiments are found when the substitutents are modified. In the second set of molecules, the phenyl rings is replaced with an oxazole, thiazole (**2**), or benzo[*b*]oxazole unit (**3**) in line with the experimental work by Bello and Griffiths where considerably longer excitation wavelengths were found than for the first set.[54] This set was chosen because we would like to investigate molecules with as long excitation wavelength as possible.

The excitation energies of the $n \rightarrow \pi^*$ transition, the S_1 state, are presented in Table 5 for all the molecules. It is found that the S_1 excitation energies are almost constant for this set of molecules and the variation is less than 0.3 eV. Furthermore, the RPA(D) results are as close as 0.3 eV to the SOPPA results, and this difference is also almost constant. Thus it seems like a difficult task to tune the S_1 excitation energy by substitution of functional groups, at least at the para position. Apparently, the energy levels of both the n and the π^* orbitals are more or less unaffected by the substitutions carried out here. In Table 5, it is also noted that the S_1 excitation to a large extent is dominated by single-electron excitations.

The $\pi \rightarrow \pi^*$ excitation energies are presented in Table 6 and in contrast to the S_1 states they show much more dependence on the molecule. Since it was assumed previously that the π^* orbital was approximately the same for the different molecules, it is the π orbital that is modified by the substitutions. For the 4-substituted azobenzenes, we find an excellent agreement between our calculations and experiments.[13,14,33,55] The differences are smaller than 0.1 eV, and especially important, we are also able to reproduce the shift in excitation energy for the electron donors (+M groups) -OH, -OCH_3, and -NH_2. Furthermore, the largest shift in excitation energy is found for the amino group which lowers the excitation energy 0.67 eV compared to TAB. Also for the S_2 states, the RPA(D) results give the same trends as the SOPPA calculations even though RPA(D) gives excitation energies that are approximately 0.7 eV too high compared to experiment. It is interesting to note that for the +M groups the difference between RPA(D) and SOPPA results is slightly larger. Nonetheless, also the RPA(D) method is suitable for a systematic investigation of the lowest singlet states in the azobenzenes. For the only disubstituted azobenzene included in this work, 4-methoxy-4'-cyanoazobenzene **(1 g)**, we also find excellent agreement with experiment. The S_2 excitation energy is calculated to be 3.33 eV in comparison to the experimental absorption maxima at 3.40 eV.[33] It should be noted that the experimental value has been measured for a polymer film where the azobenzene dye is placed in the side chain of the polymer. Furthermore, it is interesting to note that the difference between the S_2 excitation energy of the SOPPA and RPA(D) methods has increased slightly compared to the monosubstituted azobenzenes. Also for the S_2 excitations, it is noted that they are dominated by single-electron excitations.

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Table 5. Excitation Energies (eV) of the $S_1(n \rightarrow \pi^*)$ State with Use of the [3s2p(1d)/2s] Basis

	R_1	R_2	SE(%)[a]	SOPPA[b]	RPA(D)	SOPPA-RPA(D)
1a	H	H	92.5	2.49	2.77	−0.28
1b	CN	H	92.4	2.44	2.72	−0.28
1c	CH_3	H	92.5	2.52	2.79	−0.27
1d	OH	H	92.5	2.56	2.83	−0.27
1e	OCH_3	H	92.5	2.55	2.82	−0.27
1f	NH_2	H	92.5	2.59	2.87	−0.28
1g	OCH_3	CN	92.5	2.49	2.78	−0.29

	X	R_1	R_3	R_4	SE (%)	SOPPA	RPA(D)	SOPPA-RPA(D)
2a	O	H	H	H	92.5	2.55	2.82	−0.27
2b	O	NH_2	H	H	92.5	2.65	2.92	−0.27
2c	O	H	H	Cl	92.5	2.53	2.80	−0.27
2d	O	H	CHO	H	92.3	2.47	2.75	−0.28
2e	O	H	$CH{=}CH_2$	H	92.4	2.55	2.82	−0.27
3	O	H			92.4	2.50	2.78	−0.28
2f	S	H	H	H	92.2	2.50	2.79	−0.29
2g	S	NH_2	H	H	92.1	2.59	2.89	−0.30
2h	S	NH_2	CHO	Cl	91.8	2.49	2.81	−0.32

[a] Single-electron character of the excitation. [b] All the oscillator strengths are 0.00 in both the length and the velocity representations.

Table 6. Excitation Energies (eV) and Oscillator Strenghts[a] of the $S_2(\pi \rightarrow \pi^*)$ State with Use of the [3s2p(1d)/2s] Basis

	R_1	R_2	SE (%)[b]	SOPPA	RPA(D)	SOPPA-RPA(D)	exptl
1a	H	H	90.0	3.90 (0.70/0.61)	4.56	−0.66	3.86[c]
1b	CN	H	89.8	3.82 (0.80/0.71)	4.51	−0.69	3.81[c]
1c	CH_3	H	89.9	3.82 (0.74/0.64)	4.48	−0.66	3.75[c]
1d	OH	H	89.2	3.60 (0.73/0.59)	4.36	−0.76	3.56[d]
1e	OCH_3	H	88.8	3.51 (0.73/0.58)	4.32	−0.81	3.56[c]
1f	NH_2	H	88.3	3.23 (0.75/0.58)	4.06	−0.73	3.19[d]
1g	OCH_3	CN	88.3	3.33 (0.79/0.62)	4.21	−0.88	3.40[e]

	X	R_1	R_3	R_4	SE(%)	SOPPA	RPA(D)	SOPPA-RPA(D)
2a	O	H	H	H	89.5	3.77 (0.65/0.59)	4.43	−0.66
2b	O	NH_2	H	H	87.9	3.05 (0.76/0.58)	3.85	−0.80
2c	O	H	H	Cl	89.1	3.66 (0.64/0.57)	4.34	−0.68
2d	O	H	CHO	H	89.3	3.59 (0.76/0.69)	4.22	−0.63
2e	O	H	$CH{=}CH_2$	H	89.1	3.38 (0.60/0.54)	4.05	−0.67
3	O	H			88.9	3.61 (0.91/0.82)	4.28	−0.67
2f	S	H	H	H	89.2	3.53 (0.52/0.44)	4.18	−0.65
2g	S	NH_2	H	H	87.8	2.97 (0.76/0.55)	3.75	−0.78
2h	S	NH_2	CHO	Cl	87.3	2.64 (0.87/0.59)	3.42	−0.78

[a] The oscillator strengths in velocity and length representation are given in parentheses. [b] Single-electron character of the excitation. [c] Reference 13. [d] References 55 and 14. [e] Reference 33.

Aspects that are not included in the calculations are, for example, solvent effects and contributions from intramolecular motion. For some azobenzenes, experimental data exist for several solvents. The general trend is that the shift of the absorption maximum due to the solvent is of the same order as the difference between the experimental data and the calculations presented here.[12,56] Furthermore, an absorption spectrum is normally an average over several vibrational states even if the vibrational structure of the electronic absorption spectra of azobenzene has been studied recently.[57] These effects affect the direct comparison of calculated excitation energies and experimental absorption maxima, even if it is noted from the results of this work that the calculated and experimental results are close to each other.

If we turn to the compounds where oxazole or thiazole have been used as one of the diazo components (**2**), we find that oxazole reduces the excitation energy by 0.13 eV and thiazole by 0.37 eV, respectively, compared to azobenzene. Of the electron donors included here, the amino group had the largest effect on the $\pi \rightarrow \pi^*$ transition. For azobenzene it lowered the excitation energy by 0.67 eV and for the oxazole and thiazole diazo compounds by 0.72 and 0.56 eV, respectively. To compare with the experiments by Bello and Griffiths,[54] we have carried out calculations with R_3 = -CHO and R_4 = -Cl. These substitutions lowered the S_2 excitation energy by a few tenths of an electronvolt. It is furthermore demonstrated that a vinyl group gives a lower excitation energy than a formyl group and should thus be the preferred choice if a low excitation energy is desirable. We have also added a phenyl ring to the oxazole unit, benzo[*b*]oxazole (**3**), but that only led to minor effects on the excitation energy.

Finally, we have carried out a calculation on **2h** that is similar to one of the molecules in the experimental work in ref 54. The only difference is that we used R_1 = $-NH_2$ instead of R_1 = $-NEt_2$, and we also found an excitation energy of 2.64 eV in our calculations compared to 2.16 eV. The difference of 0.48 eV is probably due to two things. The first reason is the difference between $-NH_2$ and $-NEt_2$. Actually, Shuto calculated a difference between 4-NH_2 -4′-NO_2 -azobenzene and 4-NEt_2-4′-NO_2-azobenzene of 0.38 eV with a semiempirical method,[31]

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which almost corresponds to our difference of 0.48 eV. Another possibility is that we used the molecular geometry of thiazole for the thiazole unit and the same geometry for the azo group as in azobenzene. Nevertheless, it is demonstrated that the method applied here is capable of not only reproducing but also predicting excitation energies of azo dyes.

IV. Conclusions

In this work, we have demonstrated that ab initio methods, like the second-order polarization propagator approximation, can be used to accurately calculate singlet excitation energies of azo dyes. For example, the lowest singlet as well as triplet excitation energies of *cis*- and *trans*-azobenzene are well reproduced by our calculations. Furthermore, the calculated excitation energies to the S_2 states of substituted *trans*-azobenzenes as well as the shifts in excitation energy for different substituents are in excellent agreement with the experimental absorption maxima.

Since the method adopted here is not empirical, it is also suitable to suggest promising diazo components to be used in the development of data storage devices. In particular we find that the amino group as electron donor lowers the S_2 excitation energy considerably.

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