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Molecular Modeling Studies on the Photochemical Stability of Azo Dyes

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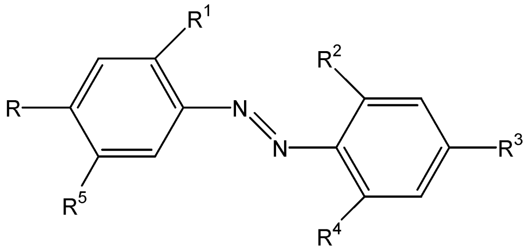
The structure and electronic properties of a series of colored azobenzenes and azothiophenes containing electron donors and attractors have been calculated with both semiempirical and ab initio methods. A reasonable correlation has been found between the predicted positions of the first and second absorption bands of the azo dyes calculated with the AM1/MECI method and the experimental values determined in methanol. The known photochemical degradation reactions of 4-dialkylaminoazobenzenes containing nitro groups in either the 2′- or 4′-position of the chromophore, which proceed via irradiation of the second absorption band, have been modeled by calculating the structures and electronic properties of the corresponding singlet and triplet states at the AM1 level. The superior photochemical stability of the 4′-nitroazobenzenes over the corresponding 2′-isomers has been rationalized in terms of the magnitude of the calculated spin densities of the azo nitrogen atoms in the second excited triplet state.

Introduction

It is well established that the vast majority of organic dyes and pigments eventually fade in the presence of sunlight. The photofading characteristics or lightfastness of a given dye depends on a number of factors including the nature of the substrate, which may be fiber, plastic, or paper, the chemical structure and electronic properties of the chromophore, as well as the wavelength and intensity of the light used for fading studies. Although there have been many studies on the lightfastness or photochemical stability of synthetic dyes the mechanism of the process is not fully understood.[1−7]

In modern applications, such as ink-jet printing, lightfastness is of critical importance as the dye is concentrated at the paper surface whereas in more conventional applications, such as textile dyeing, the dye is distributed more homogeneously through a much thicker fiber and the same degree of fading is less noticeable. Black, cyan, yellow, and magenta dyes are used in ink-jet printing, with a combination of the last three colors producing a full color printing spectrum. While dyes which have narrow absorption bands, high tinctoral strength, and no secondary visible absorptions are preferred as the colored components, because they have a brighter color, they often suffer from the disadvantage of poor lightfastness. Both the yellow and magenta dyes are generally based on the azobenzene skeleton, but the mechanism of the photofading process which gradually occurs on paper is not properly understood. While several papers have proposed mechanisms for the corresponding photoreactions of azo dyes on polyamide substrates[3,4] the reaction on nonprotein substrates has not been explored in detail and the fading products have not been established.[5]

We have recently explored the photochemical stability of a series of colored azobenzenes (**1**) and azothiophenes (**2**) containing both electron donors and attractors in methanol under anaerobic conditions using a xenon light source for irradiation.[1]



(1)

Structure	R	R^1	R^2	R^3	R^4	R^5
(a)	$N(C_2H_5)_2$	SCH_3	H	NO_2	H	H
(b)	$N(C_2H_4OH)_2$	Cl	H	Cl	NO_2	H
(c)	$N(C_2H_4OH)(C_2H_5)$	H	H	CO_2CH_3	H	H
(d)	$N(C_2H_4OH)(C_2H_5)$	H	H	H	NO_2	H
(e)	$N(C_2H_4OH)(C_2H_5)$	CH_3	H	CO_2CH_3	NO_2	H
(f)	$N(C_2H_4OH)(C_2H_5)$	H	H	Cl	NO_2	H
(g)	$N(C_2H_4OH)_2$	H	H	Cl	NO_2	H
(h)	NH_2	H	H	NO_2	H	H
(i)	$N(C_2H_4OH)(C_2H_5)$	H	H	NO_2	H	H
(j)	$N(C_2H_5)_2$	H	H	NO_2	H	H
(k)	$N(C_2H_4OH)_2$	H	H	NH_2	H	H
(l)	$N(C_2H_5)(C_2H_4CN)$	H	H	NO_2	H	H
(m)	$N(C_2H_4OH)(C_2H_5)$	H	H	NO_2	Cl	H
(n)	$N(C_2H_4OH)_2$	H	H	H	H	H
(o)	$N(C_2H_4OCOCH_3)_2$	CH_3	CN	NO_2	Br	H
(p)	$N(CH_3)_2$	H	H	NO_2	H	H
(q)	$N(C_2H_4OH)_2$	H	H	H	NO_2	
(r)	$N(CH_3)_2$	H	H	H	NO_2	H

Azobenzenes containing a donor group in one ring and an acceptor group in the other at the para positions of the chromophore were found to be the most stable, while those containing the same donor group but with the acceptor group at the 2′-position were the least stable and found to have similar lifetimes to azothiophenes. For example, 4-(*N*-ethyl-*N*-(*β*-hydroxyethyl))amino-4′-nitroazobenzene (**1i**) lost its color in 4.46 h under the anaerobic irradiation conditions employed, while the isomeric 2′-nitroazobenzene (**1d**) and 2-(4-*N*,*N*-bis(*β*-

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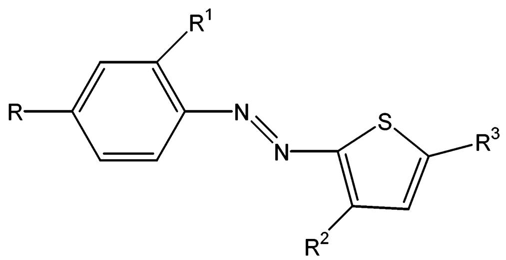
acetoxyethyl)aminophenylazo)-3,5-dinitrothiophene (**2a**) lost color in 1.37 and 1.36 h, respectively, under the same conditions.



(2)

Structure	R	R^1	R^2	R^3
(a)	$N(C_2H_4OCOCH_3)_2$	H	NO_2	NO_2
(b)	$N(C_2H_5)_2$	$NHCOCH_3$	NO_2	NO_2

The photofading reaction or loss of color in each case was attributed to the irradiation of the second absorption band alone as the reaction is inhibited in methanol if ultraviolet filters, which eliminate light below 350 nm, are placed in front of the light source.[1] It follows that the second excited singlet state of the respective dye is initially implicated in the photofading mechanism.[1] A previous study on 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**), also in methanol, came to the same conclusion and showed that additives such as benzene, fluorene, and naphthalene photosensitized the degradation reaction while anthracene was found to be wholly ineffective.[8] In our studies, the lifetime of all of the azo dyes was found to increase substantially in the presence of oxygen, supporting previous studies which have proposed that an azo triplet state is the reactive species in the photochemical degradation reaction.[8] This is believed to behave as a biradical and abstract hydrogen from the solvent as the relative rate of photofading increases sharply in moving from methanol to propan-2-ol.[1]

In the present studies, we have attempted to rationalize the experimental photochemical stabilities of the azo dyes by calculating their structures and electronic properties not only in the ground state but also in the first and second excited states. A total of 16 azobenzenes (**1**) and phenylazothiophenes (**2**) containing a variety of donor and acceptor groups in each of the aromatic rings were calculated in these studies.

Methods of Calculation

Molecular orbital calculations were carried out on empirical structures for the azobenzenes (**1**) and azothiophenes (**2**) by using the AM1[9] and PM3[10] methods of the MOPAC 93 program[11] in methanol, using the COSMO method[12,13,14] with full optimization of all bond lengths, angles, and torsion angles except where stated otherwise. The atom numbering convention adopted is shown in Charts 1−3. The following keywords were used to optimize the ground state in methanol at the AM1 level: prec am1 ef xyz geo-ok eps = 32.7. Excited-state geometries were calculated by adding additional keywords, c.i. = 6 singlet (or triplet), root = 2 (first excited state), or root = 3 (second excited state), and open(2,2), to specify that there are two electrons in two levels.

Once the ground and excited state optimized structures had been obtained the energies were refined by using the multielectron configuration interaction (MECI) treatment in MOPAC 93, which considers up to 4900 configurations generated between all combinations of up to eight electrons in the four highest occupied and four lowest unoccupied molecular orbitals. For example, spectroscopic calculations were carried out first on the optimized ground-state geometry in methanol with use of the keywords am1 prec 1scf xyz eps = 32.7 ef geo-ok meci singlet c.i. = 4 (or 6 or 8) root = 1 vectors let large, to give the refined singlet ground-state energy, and then the transition energy evaluated from the difference between this value and the first excited singlet state energy calculated by using the same keywords except root = 2 and open(2,2) were added. The second excited state was evaluated by the same method but with root = 3. Electron spin distributions were analyzed by adding the keyword esr.

More accurate reference calculations of the ground state were carried out with the RHF/6-31G** basis sets[15] of the GAMESS program.[16] Density functional calculations were carried out with the Becke three-parameter exchange functional[17] and the nonlocal correlation functional of Lee, Yang, and Parr at the B3LYP/6-31G** level.[18]

The spectra were calculated also by using a version of the CNDO/S method,[19] which has been specifically developed for dyes and pigments,[21] using a spectroscopic constant of 0.65, a core coefficient of 0.33, and 50 singly excited configurations taken from the transitions between seven and eight occupied and unoccupied molecular orbitals. Molecules and crystal structures were displayed and analyzed with the SYBYL molecular modeling package.[20]

Results and Discussion

Structural Aspects. We have previously calculated the geometry of related donor−acceptor azobenzenes such as 4-(*N*,*N*-dimethylamino)-4′-nitroazobenzene (**1p**) at various levels of theory in the gas phase and compared the results with experimental data. Crystallographic data show that most simple azobenzenes containing donor−acceptor groups in the para positions are essentially planar,[21,22] with torsion angles between the aromatic rings and the plane of the azo group ranging from 1.2° to 4.8°. In contrast, our AM1 calculations on **1p** gave a nonplanar conformation, with the nitrophenyl ring twisted by 37.3° to the plane formed between the azo group and the donor phenyl ring. However, calculations where the heavy atoms of the dye were constrained to lie in the same plane produced very similar heats of formation to the twisted conformation, with identical bond lengths found in each calculated structure. For example, the $-N{=}N-$, $Ar-N(CH_3)_2$, and $Ar-NO_2$ bond lengths of **1p** were calculated to be 1.232, 1.396, and 1.485 Å compared with expected values of around 1.273, 1.369, and 1.461 Å, respectively, based on crystallographic data.[21,22] Ab initio calculations on the same molecule at the 3-21G level gave a planar structure, but the $-N{=}N-$ bond length was still predicted to be too short at 1.244 Å.[21,22]

In contrast, crystallographic evidence strongly suggests that related 2′-nitroazobenzenes such as **1b** and **1d**−**g** are nonplanar. For example, in the closely related 4-(*N*,*N*-bis(β-hydroxyethyl)-amino)-2′-nitroazobenzene (**1q**), the donor ring and the azo group are coplanar, but the acceptor ring is twisted relative to this plane by 44.5°, and the nitro group is twisted by a further 27.6° relative to the plane of the acceptor ring.[23] In solution these torsion angles may be less pronounced, but nonetheless, the molecule is essentially nonplanar because of the large electronic and repulsive interaction between the lone pair of electrons residing on one of the oxygen atoms of the nitro group, and those residing on the nearby nitrogen atom of the azo linkage. Previous AM1 calculations on the simpler 4-(*N*,*N*-dimethylamino)-2′-nitroazobenzene (**1r**) in the gas phase gave a nonplanar structure with both aromatic rings twisted in different directions around the central $-C-N{=}N-C-$ plane by 15.6° and −24.3°, respectively, and the nitro group twisted by 50.1° relative to the acceptor ring.[21]

TABLE 1: Summary of Calculated Bond Lengths and Torsion Angles for the AM1 Structures of Both the Azobenzenes (1) and Azothiophenes (2) in Methanol (eps = 32.7)[a]

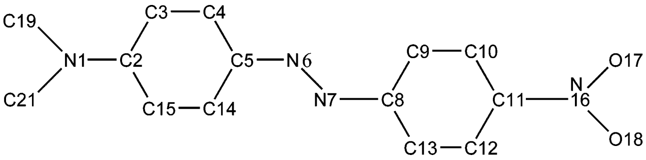
	bond lengths						torsion angles			
dye	N1−C2	C5−N6	N6−N7	N7−C8	C11−N16	N16−O17	N6N7C8C9	C14C5N6N7	ΔH_f	ΔE
1a	1.379	1.426	1.231	1.439	1.475	1.207	−50.7	18.5	80.44	1.02
1h	1.389	1.426	1.231	1.439	1.475	1.207	51.3	−0.1	79.23	1.76
1i	1.393	1.427	1.231	1.439	1.475	1.207	47.1	−10.4	30.26	0.83
1j	1.379	1.423	1.232	1.438	1.475	1.207	46.2	−7.9	81.48	1.12
1*l*	1.395	1.428	1.230	1.439	1.477	1.206	−55.6	20.4	25.65	1.54
1m	1.399	1.427	1.230	1.439	1.475	1.207	−49.6	3.1	107.6	1.80

	bond lengths						torsion angles			
dye	N1−C2	C5−N6	N6−N7	N7−C8	C13−N16	N16−O17	N6N7C8C9	C8C13N16O17	ΔH_f	ΔE
1b	1.381	1.426	1.229	1.438	1.480	1.204	−81.7	−33.0	−26.75	2.05
1d	1.390	1.426	1.230	1.438	1.480	1.204	−63.2	−38.9	31.95	2.02
1e	1.396	1.427	1.229	1.434	1.490	1.203	−69.5	−36.7	−61.80	2.41
1f	1.384	1.424	1.229	1.438	1.480	1.204	−84.6	−33.2	28.25	2.15
1g	1.390	1.426	1.229	1.439	1.479	1.205	−76.5	−34.4	−23.33	2.20

	bond lengths						torsion angles			
dye	N1−C2	C5−N6	N6−N7	N7−C8	C9−N16	N16−O17	N6N7C8C9	C8C9N16O17	ΔH_f	ΔE
2a	1.395	1.425	1.233	1.421	1.452	1.205	46.2	−33.5	−102.5	1.90
2b	1.376	1.417	1.235	1.419	1.442	1.207	32.6	−36.2	37.70	1.30

[a] Bond lengths in Å; torsions angles in deg; ΔH_f is the heat of formation in kcal mol^{-1}; ΔE is the difference in energy in kcal mol^{-1} between the freely optimized structure and an optimization where the heavy atoms of the phenylazo group, the acceptor phenyl or thiophene ring, and the atoms N1, C19, and C21 are all constrained to lie in the same plane.

CHART 1: Atom Numbering System for the 4′-nitroazobenzenes (1)



In these studies, we have calculated the structures and properties of all the azo dyes **1** and **2**, whose photochemical stability we have previously assessed in methanol, using the AM1 method coupled with some reference calculations performed at a higher level. The numbering scheme shown in Chart 1 was adopted for the 4′-nitroazobenzenes. The unconstrained AM1 optimizations on the 4′-nitroazobenzenes such as **1h**−**j** and **1*l***,**m** gave nonplanar structures in methanol (similar results were obtained in the gas phase) with the donor ring twisted by 0.1° to 20.4° relative to the plane of the central azo group, C5−N6−N7−C8, while the acceptor ring is always twisted to a larger degree with the torsion angle, N6−N7−C8−C9, ranging from 46.2° to 70.8° (Table 1). For example, while both the donor ring and acceptor rings of 4-(*N*-ethyl-*N*-(*β*-hydroxyethyl))amino-4′-nitroazobenzene (**1i**) are twisted by −10.4° and 47.1° relative to the central azo plane, C5−N6−N7−C8, only the acceptor ring of 4-amino-4′-nitroazobenzene (**1h**) is out of plane and twisted by 51.3° relative to the same axis. However, when the atoms of the azobenzene skeleton, and N1, C19, and C21 of the donor group, are constrained to lie in the same plane, the key bond lengths N1−C2, N6−N7, and C11−N16 of all the 4′-nitroazobenzenes are only marginally different from those obtained from the unconstrained optimization with the molecular energy raised by only 0.8 to 1.80 kcal mol^{-1} (Table 1). There seems little doubt from the crystallographic data,[21,22] and from these results in methanol coupled with our previous results in the gas phase,[21] that it is necessary to constrain the heavy atoms to produce a reliable structure when using the AM1 method.

In contrast, the unconstrained optimizations in methanol at the PM3 level produce an essentially planar azobenzene skeleton but the nitrogen atom, N1, at the donor group is sp^3 hybridized with the alkyl groups lying well below the molecular plane, and the N1−C2 bond length is substantially overestimated. For example, in **1i**, the alkyl groups at C19 and C21 are predicted to lie 20.3° below the molecular plane, and the calculated N1−C2 distance at 1.438 Å (Table 2) is far too long by comparison with experimental data on related structures. At the AM1 level these values are 5.1° and 1.393 Å and much closer both to the expected values derived from crystallographic data[21,22] and to more accurate calculations on the same structure (**1i**) both at the RHF/6-31G** level and at the DFT/B3LYP/6-31G** level which yield an essentially planar structure with a N1−C2 bond length of 1.374 and 1.377 Å, respectively (Table 2).

However, in the 2′-nitroazobenzenes, the molecules are not planar because of clash between one of the azo nitrogens and the adjacent oxygen on the nitro group as described earlier. The numbering scheme in Chart 2 was adopted for these structures.

As before, the unconstrained AM1 optimizations also gave nonplanar structures in methanol with the acceptor ring predicted to be considerably more twisted than that found in the 4′-nitroazobenzenes as shown by the torsion angle N6−N7−C8−C9, which ranges from 63.2° to 84.6° (Table 2). Additionally, the pendant nitro group is also twisted relative to the plane of the acceptor ring so that the calculated torsion angle C8−C13−N16−O17 ranges from 33.0° to 60.6° (Table 1). For example, the donor and acceptor rings of 4-(*N*-ethyl-*N*-(*β*-hydroxyethyl))amino-2′-nitroazobenzene (**1d**) are twisted by 11.5° and 63.2°, respectively, relative to the central azo group, while the pendant nitro group is twisted by 38.9° relative to the acceptor ring. At the PM3 level in methanol, the corresponding vales are 18.4° and 60.0° for the phenyl rings and 41.8° for the nitro group (Table 2). Again, the PM3 method generates an sp^3 hybridized amino group with the alkyl groups at C19 and C21 lying 22.2° below the molecular plane with a calculated N1−C2 distance at 1.435 Å compared with values of 10.2° and 1.390 Å, respectively, for the AM1 structure (Table 2).

Ab intio calculations at the RHF/6-31G** level show that the acceptor ring is twisted by 36.3° relative to the central azo

TABLE 2: Selected Structural Data for 4′-Nitroazobenzene (1i) and 2′-Nitroazobenzene (1d) Calculated by Using the PM3 and AM1 Methods in Methanol (eps = 32.7) Compared with RHF Results at the 6-31G Level and DFT Results at the B3LYP/6-31G** Level in the Gas Phase**[a]

	1i					1d			
parameter	PM3	AM1	AM1[b]	RHF/ 6-31G**	B3LYP/ 6−31G**	PM3	AM1	RHF/ 6-31G**	B3LYP// 6−31G**
bond lengths									
N1−C2	1.438	1.393	1.382	1.374	1.377	1.435	1.390	1.381	1.381
C5−N6	1.442	1.427	1.421	1.404	1.395	1.439	1.426	1.406	1.398
N6−N7	1.230	1.231	1.234	1.224	1.270	1.231	1.230	1.222	1.267
N7−C8	1.451	1.439	1.437	1.419	1.413	1.452	1.438	1.416	1.409
C11−N16	1.470	1.475	1.475	1.456	1.456				
C13−N16						1.475	1.480	1.461	1.473
N16−O17	1.223	1.207	1.207	1.194	1.233	1.220	1.204	1.296	1.227
N1−C19	1.489	1.449	1.449	1.449	1.459	1.487	1.446	1.456	1.463
bond angles									
C5N6N7	120.5	120.6	120.5	116.6	115.6	120.9	120.7	116.8	115.8
N6N7C8	118.9	118.9	119.5	114.9	114.1	118.7	118.8	113.9	113.6
torsional angles									
C14C5N6N7	0.5	−10.4	0.0	−0.1	−1.6	18.4	11.5	1.10	3.90
N6N7C8C9	−0.7	47.1	0.0	0.1	−2.8	60.0	−63.2	36.3	32.0
C10C11N16O17	0.1	0.6	0.0	0.0	−1.4				
C8C13N16O17						41.8	−38.9	47.6	45.9
C5N6N7C8	−179.9	−179.6	180.0	180.0	179.3	−179.2	178.5	179.5	177.8
ΔH_f	−3.11	30.26	31.09	-	-	0.92	31.95		
μ	8.52	9.94	8.47	10.17	12.13	6.57	5.88	3.68	4.19

[a] Bond lengths in Å; torsions angles in deg; ΔH_f is the heat of formation in kcal mol^{-1}; μ is the dipole moment in D. [b] Optimization with the heavy atoms of the azobenzene skeleton and atoms N1, C19, and C21 all constrained to lie in the same plane.

CHART 2: Atom Numbering System for the 2′-nitroazobenzenes (1)

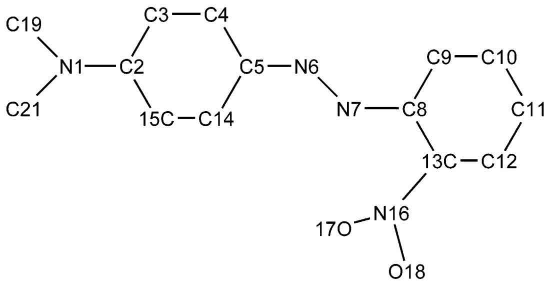
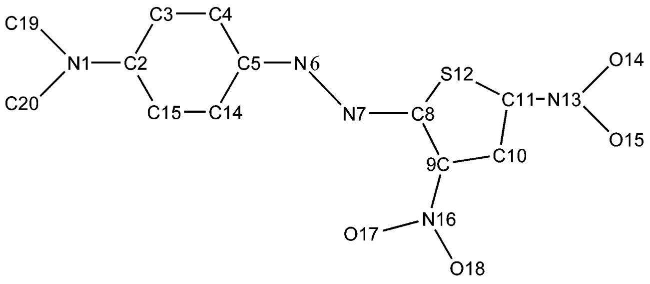


CHART 3: Atom Numbering System for the Azothiophenes (2)



group, the pendant nitro group is twisted by 47.6° relative to the attached ring, and while the N1−C2 bond length at 1.381 Å is similar to that found in the related crystal structure, 4-*N*,*N*-bis(β-hydroxyethyl)amino-2′-nitroazobenzene (**1q**), the N6−N7 distance at 1.222 Å is too short (Table 2). However, better results are obtained by using density functional theory at the B3LYP/6-31G** level with corresponding values of 32.0° and 45.9° for the same torsion angles, and 1.381 and 1.267 Å for the same bond lengths, respectively (Table 2), which compare with values of 44.5° and 27.6°, and 1.369 and 1.263 Å, respectively, in the well-resolved crystal structure of **1q**. The crystallographic data and calculated results therefore strongly suggest that the 2′-nitroazobenzenes are twisted. As the AM1 method gave better results overall than the PM3 method, it was subsequently employed to calculate the excited-state structures of all the azobenzenes (see later).

As far as the geometry of azothiophenes **2** is concerned, we have previously calculated the structure of **2a** in the gas phase using the AM1 and PM3 methods and shown that a twisted structure results where the thiophene ring is approximately orthogonal to the plane of the phenylazo group.[24] However, when the heavy atoms of chromophore **2a** were constrained to lie in the same plane during the optimization, the resulting structure was only 1.4 kcal mol^{-1} higher in energy with calculated C−S, N═N, and C−NO$_2$ bond lengths which were consistent with those found experimentally. Furthermore, previous calculations on the structure of **2b** at the STO-3G level have shown that this molecule is essentially planar.[25] In these studies, we find that the optimized structures of the two azothiophenes **2a**,**b** calculated in methanol using the AM1 method are also nonplanar with the thiophene ring twisted by 32.6° to 46.2° relative to the plane of the central azo group, C5−N6−N7−C8 (Table 1), and the nitro group is also twisted by 33.5° to 36.2° relative to the plane of the thiophene ring (Table 1). However, when the heavy atoms are constrained, sensible geometries are obtained with almost identical bond lengths to the freely optimized structures with an energy penalty of only 1.30 to 1.90 kcal mol^{-1} (Table 1). The numbering scheme in Chart 3 was adopted for these structures.

Excited-State Calculations. We have demonstrated that the photochemical degradation reaction of the azo dyes **1** and **2** is inhibited in methanol if ultraviolet filters which eliminate light below 350 nm are placed in front of the light source.[1] The reaction is thought to proceed therefore by absorption of a photon in the region of the second absorption band at 270−320 nm (Table 3) resulting in a rearrangement of electrons to form the second excited singlet state (S$_2$). Relaxation of the geometry follows quickly via a vibrational cascade to generate a lower energy relaxed singlet state (S$_2$R), which can then return to its ground state by either internal conversion (IC) or fluorescence.[6] In a competing mechanism, the second singlet state is converted to an excited triplet state by intersystem

TABLE 3: Experimental and Calculated Absorption Spectra and Optimized Excited State Singlet and Triplet State Energies of the Azo Dyes 1 and 2 Compared with Their Half-Lives in Oxygenated Methanol[a]

	exptl		calcd			relative energies				
dye	λ_1	λ_2	λ_{1A}	λ_{2A}	λ_{1C}	S_2-S_0R	S_2R-S_0R	T_2R-S_0R	T_1R-S_0R	$\tau_{1/2}°$
1a	513	307	471	429	482	59.05				11.6
1b	456	291	443	302	457	73.71				3.83
1c	445	277	436	283	443	82.80	64.34	68.59	32.16	12.4
1d	448	274	439	301	446	76.44	63.08	59.31	29.12	3.52
1e	495	289	467	303	465	74.36	64.49	68.25	34.38	4.77
1f	465	279	456	304	459	75.74	60.30	59.84	31.56	2.34
1g	438	287	420	296	446	76.30	61.50	58.42	31.80	3.84
1h	436	275	519	297	425	77.62	62.10	57.38	27.92	10.5
1i	482	286	495	284	452	82.70	61.81	57.46	32.96	12.7
1j	488	285	518	292	452	80.22	62.34	62.25	28.52	
1k	445	318	395	328	449	81.06	60.72	62.85	30.07	15.5
1*l*	456	282	502	285	443	80.25				16.5
1m	500	286	503	288	463	80.98				13.6
1n	409	259	383	279	410	87.57	68.70	68.64	49.10	8.33
2a	619	287	518	331	528	71.99	68.96	63.37		1.82
2b	613	307	514	336	569	70.48	65.51	63.97		3.47

[a] λ_1 and λ_2 are the experimental first and second absorption bands in methanol (nm); λ_{1A} and λ_{2A} are the calculated values in methanol at the AM1/MECI level (c.i. = 4); λ_{1C} is the calculated value at the CNDOVS level; S_2, S_2R, T_2R, and T_1R are the heats of formation (kcal mol^{-1}) of the excited-state species (see text) calculated at the AM1/MECI level (c.i. = 6); $\tau_{1/2}°$ is the half-life of the dye in oxygenated methanol (h).

crossing (ISC) and rearrangement of the geometry to form a lower energy relaxed triplet state (T_2R). This in turn can either revert to the ground state either by intersystem crossing or by phosphorescence[6,26] or undergo a chemical reaction resulting in photodegradation. However, the possibility that another mechanism is operating that involves the conversion of the second excited triplet state (T_2R) of the azobenzene to the lower energy first excited triplet state (T_1R) by internal conversion cannot be ruled out entirely. The first triplet state, T_1R, if formed by this route, could in principle behave as the reactive species rather than the second triplet state, T_2R (see later). The proportion of the second singlet state that converts to a reactive triplet state, rather than reverting to the ground state via internal conversion, will depend on the electronic structure and properties of the azo dye.

There seems to be little doubt from previous studies that the photdegradation reactions of azobenzenes in methanol proceed via their triplet states.[8,27] The marked increase in lifetime that we found for azo dyes **1** and **2** after irradiation in the presence of oxygen is supportive. For example, the lifetime of 4-(*N*-ethyl-*N*-(*β*-hydroxyethyl))amino-4′-nitroazobenzene (**1i**) increases from 4.46 h under anaerobic conditions in methanol to 18.8 h when the solution is saturated with oxygen. Oxygen, which is a triplet in its ground state, is thought to readily quench the excited triplet state of the azo dye to form the ground state (S_0) and generate singlet oxygen, i.e.

$$[R^1{-}N{=}N{-}R^2]^{3}{*} + O_2{}^{3} \rightarrow R^1{-}N{=}N{-}R^2 + O_2{}^{1} \quad (1)$$

The triplet states of polar organic molecules are well-known to react with hydroxylic solvents and abstract hydrogen.[28] For example, the triplet state of benzophenone readily abstracts hydrogen from propan-2-ol to form a ketyl radical that can either dimerize to form benzpinacol or abstract another hydrogen atom from the solvent to form benzhydrol.[29]

$$[Ph_2C{=}O]^{3}{*} + CHMe_2OH \rightarrow [Ph_2COH]^{\bullet} + {}^{\bullet}CMe_2OH \quad (2)$$

A similar process almost certainly occurs with the donor−acceptor azo dyes **1** and **2** with either nitrogen, N6 or N7, abstracting hydrogen to form a less colored hydrazo radical and a hydroxymethyl radical (eqs 3 and 4).[1]

$$[R^1{-}N{=}N{-}R^2]^{3}{*} + CH_3OH \rightarrow R^1{-}NH{-}N^{\bullet}{-}R^2 + {}^{\bullet}CH_2OH \quad (3)$$

$$[R^1{-}N{=}N{-}R^2]^{3}{*} + CH_3OH \rightarrow R^1{-}N^{\bullet}{-}NH{-}R^2 + {}^{\bullet}CH_2OH \quad (4)$$

The hydrazo radicals once formed can also abstract hydrogen from the solvent in the following way to form hydrazobenzenes

$$R^1{-}NH{-}N^{\bullet}{-}R^2 + CH_3OH \rightarrow R^1{-}NH{-}NH{-}R^2 + {}^{\bullet}CH_2OH \quad (5)$$

For example, irradiation of 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**) in methanol in the absence of air produces the corresponding hydazobenzene as an intermediate product.[8,27] This subsequently reacts with other radicals present in solution to eventually form 4-(*N*,*N*-diethylamino)aniline and 4-nitroaniline.[8,27]

In these studies we have calculated all the possible excited-state species involved in the photodegradation reaction in methanol using the AM1 method. The optimized ground-state geometry of the azo dyes, S_0R, was used to calculate both the S_1 and S_2 states, using the MECI treatment (see later). The S_1R, T_1R, S_2R, and T_2R structures were obtained by full optimization of their geometries by using a limited CI treatment involving single excitations only with two of the electrons assigned to two separate levels and specified as either paired (singlet) or unpaired (triplet). Again, the energies of each structure were refined by using the MECI treatment.

Transition Energies. Both the 4-dialkylaminoazobenzenes (**1**) and the 4-dialkylaminophenylazothiophenes (**2**) generally show two main absorptions in the 259- to 619-nm region of the spectrum in methanol (Table 3). The presence or absence of an acceptor substituent in the right-hand ring of the azobenzene strongly influences the position of the long wave absorption. For example, 4-*N*,*N*-bis(*β*-hydroxyethyl)aminoazobenzene (**1n**), which has no substituent in the acceptor ring, absorbs at 409 nm in methanol while 4-(*N*-ethyl-*N*-(*β*-hydroxyethyl))amino-2′-chloro-4′-nitroazobenzene (**1m**), which has two substituents in the acceptor ring, absorbs at 500 nm (Table 3). The position of the substituent in the right-hand ring also has a pronounced effect. Thus while 4-(*N*-ethyl-*N*-(β-hydroxyethyl))-amino-4′-nitroazobenzene (**1i**) absorbs at 482 nm, the corresponding isomeric 2′-nitroazobenzene **1d** absorbs at 448 nm (Table 3). Generally, the simple donor acceptor azobenzenes **1a**−**m** range in color from yellow to red in methanol with absorption maxima ranging from 436 to 513 nm.[30] However, the azothiophene dyes (**2**) examined are blue and absorb at the longer wavelengths of 613−619 nm (Table 3) primarily because of the presence of two electron attractors in the thiophene ring coupled with the capacity of the sulfur atom to act as a further electron attractor because of its vacant d-orbitals.[31]

In contrast, the position of the second absorption band, which occurs in the region of 275 to 307 nm for most of the dyes in methanol (Table 3), is influenced less by substituents or structure than the long wavelength absorption band. For example, in moving from the structure of 4-amino-4′-nitroazobenzene (**1h**) to 2′-chloro-4′-nitroazobenzene (**1m**), the marked bathochromic shift in the first absorption band from 436 to 500 nm, respectively, is not reflected in the position of the second absorption band, which shows a much smaller shift from 275 to 286 nm (Table 3).

The calculated absorption maxima or transition energies of the dyes at the AM1 level depends on the ground-state geometry adopted for the calculation. The value of the first and second singlet states obtained (S_1 and S_2) therefore depends on a number of important structural factors such as the torsion angles of the phenyl rings and the hybridization of the amino group in the ground state structure. In general, the more planar the azo dye is, the longer the absorption wavelength, but any torsional movement of the phenyl rings from planarity usually causes a hypsochromic shift. For example, the fully optimized structure of 4-amino-4′-nitroazobenzene (**1h**), which has its acceptor phenyl ring twisted from the plane of the 4-aminophenylazo group by 37°, gives a calculated transition energy in methanol of 470 nm, compared to 519 nm for a planar structure where the heavy atoms are constrained to lie in the same plane. While the planar ground-state structure is less stable and higher in energy than the twisted conformer by 1.76 kcal mol^{-1} (Table 1), in the first excited state the reverse is true with the planar excited state now more stable or lower in energy than the twisted conformer by 5.76 kcal mol^{-1}.

While structural effects have an important influence on the calculated transition energies, the number of occupied and unoccupied molecular orbitals used in the calculation and the configuration interaction treatment adopted all have a significant effect as well. For example, 4-(*N*-ethyl-*N*-(β-hydroxyethyl))-amino-4′-nitroazobenzene (**1i**) has a total of 120 valence electrons which occupy the first 60 molecular orbitals in the ground state. The MECI treatment at the AM1 level can generate a large number of configurations depending on the number of molecular orbitals used in the calculation. In these studies, up to four occupied and four unoccupied molecular orbitals, ψ57 to ψ64, were explored in the spectroscopic calculation, which generates up to 4900 configurations involving a maximum of all the possible eight electron combinations (singlets, triplets, etc.). As an independent check, the spectra were calculated also with the CNDOVS method,[21] using 50 configurations involving single excitations only selected in order of energy from transitions between molecular orbitals ψ52 to ψ67 to ascertain whether any additional low-lying molecular orbitals contribute significantly to the transition energy of the first excited state.

The results obtained suggest that a limited MECI treatment involving four molecular orbitals, ψ59 to ψ61, gives a satisfactory account of the two main absorption bands by comparison with the experimental data in methanol (Table 3). For example, an excellent correlation is obtained between the calculated absorption bands of 4-(*N*-ethyl-*N*-(β-hydroxyethyl))amino-2′-chloro-4′-nitroazobenzene (**1m**) at 503 and 288 nm and the experimental values of 500 and 286 nm, respectively (Table 3). Other correlations are not as good, but nonetheless the method appears to successfully predict two absorptions in the correct region of the spectrum. The results for the sulfur-containing azo dyes **1a** and **2a**,**b** are less satisfactory because the AM1 method does not include the vacant "3d" orbitals of sulfur in the valence set used for calculation. However, the position of the first absorption band does show a reasonable correlation with the calculated results with use of the well-tested CNDOVS method, suggesting that the structures adopted are reliable. An increase in the size of the MECI calculation at the AM1 level from four to either six or eight molecular orbitals results in a lowering of the second excited-state energy to longer wavelengths. For example, MECI calculations on 4-amino-4′-nitroazobenzene (**1h**) with four, six, or eight molecular orbitals included gave predicted absorptions at 296, 368, and 359 nm, respectively.

Excited-State Structures. A detailed analysis of the calculated results on 4′-nitroazobenzene (**1i**) shows that the optimized structure of the first excited singlet state (S_1R) is essentially planar though there are significant bond length differences over the ground state (S_0R). Thus the N1−C2 bond length of 1.400 Å in the former is longer than the value of 1.382 Å in the latter but the C5−N6, N6−N7, N7−C8, and C11−N16 distances are shorter at 1.398, 1.210, 1.365, and 1.455 Å versus 1.422, 1.234, 1.437, and 1.475 Å, respectively (Table 4). In contrast to the planarity of the first excited singlet state (S_1R), the optimized structure of the first excited triplet state (T_1R) is twisted with the donor ring almost orthogonal to the plane of the other phenylazo group; the N1−C2 distance is much shorter at 1.355 Å and the N6−N7 bond length is longer at 1.244 Å than the values found in the singlet state structure, S_1R. The optimized structure of the corresponding second excited singlet state (S_2R) shows both donor and acceptor rings twisted by 54.2° and 49.1° relative to the C5−N6−N7−C8 axis with N1−C2, C5−N6, and C11−N7 distances of 1.416, 1.426, and 1.480 Å which are larger than those found in either of the singlet state structures, S_0R or S_1R. Surprisingly, the optimized structure of the second excited triplet state (T_2R) is almost planar with the donor and acceptor rings twisted by 4.30° and −9.60° relative to the C5−N6−N7−C8 axis (Table 4). This structure has similar bond lengths to the T_1R structure except that here the C5−N6 and N7−C8 distances are substantially shorter at 1.345 and 1.372 Å, respectively.

The same trends are apparent for the bond lengths in the corresponding 2′-nitroazobenzene **1d**. However, while the ground-state structure (S_0R) is twisted at the acceptor ring and the nitro group, the optimized structure of the first excited singlet state (S_1R) is essentially planar with similar bond lengths to the 4-isomer (**1i**) (Table 4). In contrast, the optimized structure of the first excited triplet state structure (T_1R) is again twisted, like the 4-isomer (**1i**), with one phenyl ring almost orthogonal to the central C5−N6−N7−C8 axis, but here it is the acceptor ring rather than the donor ring that is rotated by 110°. The nitro group is also twisted by 29.3° in this structure (T_1R). The optimized structure of the second excited singlet state (S_2R) shows very similar bond lengths to the 4-isomer (**1d**); both donor

TABLE 4: Calculated Structural Data for the First and Second Excited Singlet and Triplet States of Nitroazobenzenes 1i and 1d in Methanol (eps = 32.7) Compared with the Ground State Data[a]

	bond lengths (Å)						torsion angles (deg)		
dye	N1−C2	C5−N6	N6−N7	N7−C8	C11−N16	N16−O17	C14C5N6N7	N6N7C8C9	C10C11N16O17
1i									
S_0R	1.382	1.422	1.234	1.437	1.475	1.207	0	0	0
S_1R	1.400	1.398	1.210	1.365	1.455	1.209	−0.0	−0.3	0.1
T_1R	1.355	1.398	1.244	1.390	1.430	1.219	94.9	−0.2	−0.3
S_2R	1.416	1.426	1.203	1.420	1.480	1.203	−54.2	−49.1	0.3
T_2R	1.371	1.345	1.221	1.372	1.431	1.220	4.3	−9.6	−0.2

	bond lengths (Å)						torsion angles (deg)		
dye	N1−C2	C5−N6	N6−N7	N7−C8	C13−N16	N16−O17	C14C5N6N7	N6N7C8C9	C8C13N16O17
1d									
S_0R	1.390	1.426	1.230	1.438	1.480	1.204	11.5	−63.2	−38.9
S_1R	1.401	1.402	1.218	1.357	1.456	1.203	0.6	0.1	6.3
T_1R	1.376	1.340	1.261	1.432	1.480	1.202	−8.7	−110.2	−29.3
S_2R	1.415	1.428	1.207	1.432	1.488	1.199	−58.5	24.7	−44.5
T_2R	1.365	1.373	1.211	1.357	1.425	1.222	−5.1	−0.8	0.1

[a] Bond lengths in Å; torsions angles in deg.

and acceptor rings are again twisted but here in opposite directions by −58.5° and 24.7° relative to the C5−N6−N7−C8 plane. A similar pattern emerges for the optimized structure of the second excited triplet state (T_2R), which is approximately planar with torsion angles of −5.1° and −0.8° between the central azo group and donor and acceptor rings, respectively (Table 4). Additionally, the nitro group in this structure (T_2R) is predicted to be coplanar with the acceptor ring with the overall torsion angles similar to the first excited singlet structure (S_1R). Exactly the same trends in the ring torsion angles are apparent for the S_1R and T_2R structures of the 4-isomer (**1d**).

Triplet-State Energies. We have shown that the photochemical stability of azo dyes **1** depends on their chemical structure. Thus those dyes containing an electron attractor at the 4′-position of the right-hand ring of the azobenzene, such as **1h**−**k**, are more stable than either those containing the same substituent in the 2′-position, such as **1d**−**g**, or azothiophenes **2a**,**b**. While the first excited singlet state (S_1) is very sensitive to substituent and conformational effects, the corresponding second excited state (S_2) is not (Table 3). Although the use of a limited MECI treatment (c.i. = 4) appears to be adequate for the energy of the singlet states which are based on the ground-state structure, this is not true for the energies of the relaxed second singlet (S_2R) and triplet states (T_2R) where their relative energies differ when the number of included molecular orbitals (MOs) is increased. With only four MOs included in the calculation for the azo dyes **1d**,**f**,**i**,**n**,**o**, the T_2R state is higher in energy than the corresponding S_2R state, whereas with eight MOs included in the calculation, they are lower in energy. For example, 2′-nitroazobenzene **1d** has calculated S_2R and T_2R values of 63.7 and 65.0 kcal mol^{-1} (c.i. = 4), 63.1 and 59.3 kcal mol^{-1} (c.i. = 6), and 62.2 and 60.0 kcal mol^{-1} (c.i. = 8), all relative to the S_0R ground state. As the inclusion of six molecular orbitals in the MECI calculation appeared to be satisfactory, the remaining molecules were assessed and analyzed at this level of accuracy (Table 3). In all cases the energies of the relaxed second singlet (S_2R) and triplet states (T_2R) discussed above are predicted to be significantly lower than the initial excited state (S_2) by around 10 to 25 kcal mol^{-1} as expected (Table 3). For example, the T_2R states of 2′-nitroazobenzene **1d** and isomeric 4′-nitroazobenzene **1i** lie 17.1 and 25.2 kcal mol^{-1}, respectively, below the corresponding S_2 state, and 3.77 and 4.35 kcal mol^{-1} below the S_2R state (Table 3).

Intersystem crossing from the second singlet state to an intermediate triplet state will occur at some point between the S_2 and S_2R levels on one hand and the T_2 and T_2R levels on the other where the potential energy surfaces of the singlet and triplet states intersect at a common geometry.[32] Because the excited-state geometries of the S_2R and T_2R structures are markedly different in terms of the key bond lengths and ring torsion angles (see above), it is unlikely that intersystem crossing will occur near these energy minima. Clearly, the energy of the T_2 state would be expected to show a strong conformational dependence, particularly for 2-nitroazobenzenes **1d**−**g** where there are large steric interactions between the nitro group and the adjacent azo nitrogen (see above). Our results suggest that the singlet−triplet conversion occurs near the S_2 level where the bond lengths and the ring torsion angles of this ground-state structure are similar to the T_2R structure (Table 4). However, there appears to be no obvious correlation between the calculated energies of the species formed from the initial S_2 state and the measured photochemical stability of the azo dyes as assessed by their half-lives in oxygenated methanol (Table 3).

The possibility exists, however, that the second excited triplet state (T_2R) of the azobenzene changes to the lower energy and longer lived first excited triplet state (T_1R) by internal conversion. Although T_1R could therefore behave as the reactive species rather than the second triplet state, T_2R, the calculated results are not supportive. Our results suggest that the first triplet lies around 29 to 34 kcal mol^{-1} above the ground state (Table 3). These values appear to be reasonably consistent with the values of around 40 kcal mol^{-1} obtained for a series of azobenzenes such as **1r** determined experimentally in viscous solution by laser flash photolysis.[33] The second triplet state, however, is calculated to be at least 57 kcal mol^{-1} above the ground state (Table 3) in line with indirect evaluations of azobenzene **1j**, which places the energy between 47 and 61 kcal mol^{-1} (see below).

The formation and reaction of the second triplet state (T_2R) is probably responsible for the photodegradation reactions observed for the following two reasons. First, no discernible photodegradation is observed on irradiation of the first absorption band over many hours,[1] which would be expected to yield some of the triplet species by intersystem crossing from S_1R to T_1R. Second, previous irradiation studies on 4-(*N*,*N*-diethylamino)-4′-nitroazobenzene (**1j**), also in methanol, have shown that benzene, fluorene, and naphthalene are effective photosensitizers for the degradation reaction, while anthracene is wholly ineffective.[8] Because benzene, fluorene, and naphthalene

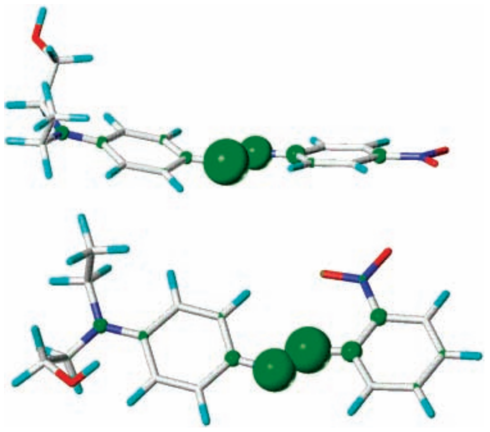


Figure 1. Structure and spin density distribution (shown as green spheres) of the second excited triplet state (T_2R) in methanol of 4′-nitroazobenzene (**1i**) (above) and isomeric 2′-nitroazobenzene (**1d**) (below).

have triplet energies of 84, 68, 61 kcal mol^{-1}, respectively,[34] which lie above the energy of the second triplet state (T_2R) of azobenzene **1j**, they are able to transfer energy and photosensitize the degradation reaction. The calculated value of 62.3 kcal mol^{-1} (Table 3) for the T_2R state of **1j** is a little high but of the right order. However, anthracene, which has a triplet energy[34] of only 47 kcal mol^{-1}, is unable to transfer energy in this way to the second triplet state (T_2R) of azobenzene **1j** though it lies above the first triplet state (T_1R), calculated at only 28.5 kcal mol^{-1} (Table 3). Experimentally, it has been established that the first excited state (T_1R) is implicated in the reversible trans−cis isomerization of azobenzenes but *not* their reduction to hydrazobenzenes.[8,27,33] The reported observation that anthracene does not photosensitize the degradation reaction coupled with the calculated energies strongly suggest therefore that the second excited triplet state is responsible for the photodegradation reactions observed.

Spin Densities. The two unpaired electrons in the second excited triplet state of all the azo dyes are thought to confer biradical behavior on the respective molecules leading to their reaction with the solvent. These electrons are not distributed uniformly throughout the molecular frame but are localized at certain atomic centers. A visual comparison of the spin densities of the two isomeric nitroazobenzenes, **1i** and **1d**, shows that there are considerable differences between the distribution of the unpaired electrons at the reactive azo nitrogen atoms. In the least reactive 2-nitroazobenzene (**1i**), the electron spin density in the second excited triplet state is partially accommodated by the attached phenyl rings (Figure 1). However, in the highly reactive 2-nitroazobenzene (**1d**), the electron spin density in the second excited triplet state is highly concentrated at the azo nitrogen atoms alone (Figure 1).

A detailed analysis of the calculated electron spin densities on the 4′-nitroazobenzene (**1i**), which has a total spin density of two, shows that around half is located at the donor nitrogen atom N1, the adjacent carbon C2, the nitrogen and oxygen atoms of the nitro group, and the azo nitrogens N6 and N7 (Table 5), with the remainder distributed over the other heavy atoms. The largest component of the spin density appears at the reactive azo nitrogen N6, which shows a value of 0.23 though the other azo nitrogen N6 also has a significant value of 0.14 (Table 5).

In contrast, a much larger component of the overall spin density is found at these atoms in the corresponding 2′-nitroazobenzene **1d**. Thus N6 and N7 show spin densities of 0.36 and 0.34, respectively, giving an overall value for the spin density of 0.70 compared with an overall value of 0.37 in the 4-isomer (**1i**) (Table 5). These results strongly suggest that the 2-isomer (**1d**) would be much more reactive than the 4-isomer (**1i**) because of the greater localization of the unpaired electron density at those centers which are thought to abstract hydrogen from the solvent as shown by eqs 3and 4. A comparison of the photochemical degradation of the azo dyes in methanol in the presence of oxygen shows that the 2′-nitroazobenzenes **1d−g** have half-lives ranging from 2.34 to 4.77 h while the 4′-nitroazobenzenes **1h−k** have corresponding values of 10.5 to 15.5 h (Table 5). The difference in spin density at the azo nitrogen atoms between the two isomers is not simply a reflection of their different geometries as both optimized structures for the second excited triplet state (T_2R) are broadly planar. Significantly, azothiophene **2a**, which is the most reactive dye of the series with a half-life of only 1.82 h, also shows a large spin density of 0.70 at the azo nitrogens N6 and N7 (Table 5).

TABLE 5: Spin Density Distributions Calculated by Using the AM1 Method for the Second Excited Triplet State (T_2R) of the Azo Dyes 1 and 2[a]

dye	N1	C2	C3	N6	N7	ΣN	C8	C11	N16	ΣO	$\tau_{1/2}°$
1d	0.12		0.16	0.36	0.34	0.70	0.13				3.52
1e	0.15		0.16	0.53	0.33	0.86	0.12				4.77
1f	0.12		0.13	0.33	0.36	0.69	0.17				2.34
1g	0.18	0.14	0.24	0.44	0.36	0.80	0.11				3.84
1h	0.11		0.10	0.23	0.10	0.33	0.25		0.15	0.14	10.5
1i	0.16	0.18	0.07	0.23	0.14	0.37	0.10	0.10	0.13	0.14	12.7
1k	0.16	0.19	0.19	0.16	0.15	0.31	0.19	0.18	0.15		15.5
2a	0.16	0.10	0.20	0.42	0.28	0.70	0.11				1.82

[a] Only spin densities which are greater than 0.05 at individual atoms are reported. ΣN is the total spin density at the azo nitrogen atoms N6 and N7, ΣO is the total spin density at oxygen atoms O17 and O18. $\tau_{1/2}°$ is the half-life of the dye in oxygenated methanol.

Thus the spin densities at the azo nitrogen atoms appear to generally distinguish between the reactivity of the two isomeric nitroazobenzenes and the azothiophene, but other factors such as the ease of intersystem crossing between the second singlet excited state and the corresponding triplet state will play an important role also.

Conclusions

The AM1/MECI/COSMO approach appears to give a satisfactory account of the ground- and excited-state properties of azo dyes **1** and **2**. The ground-state geometries of **1d** and **1i**, calculated at the semiempirical level, are similar to those calculated by using density functional theory and similar to related molecules reported in the Cambridge Structural Database. The calculated singlet state transition energies for the first and second excited states correlate reasonably well with the experimental values determined in methanol. The corresponding triplet energies also appear to be realistic based on direct and indirect experimental data for related systems. The poor photochemical stability of the 2′-nitroazobenzenes compared with the corresponding 4′-isomers is thought to be due to a greater localization of spin density at the reactive azo nitrogen atoms in the second excited triplet state.

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