J. Phys. Chem. A **2001,** *105,* 5984−5989

N,N-Dialkylanilines: The S$_1$ State Absorption Spectrum and Efficient Intramolecular Triplet−Triplet Energy Transfer to an Olefinic Bond

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Received: December 14, 2000; In Final Form: March 23, 2001

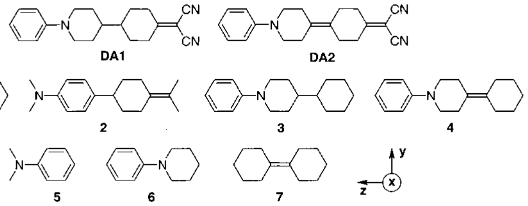
Efficient intramolecular triplet−triplet energy transfer from an *N*,*N*-dialkylanilino donor to an alkene acceptor was observed in 4-(4-(propan-2-ylidene)cyclohexyl)-*N*,*N*-dimethylaniline (**2**) and 1-phenyl-4-cyclohexylidenepiperidine (**4**) using nanosecond transient absorption spectroscopy and time-resolved microwave conductivity. This enables the unequivocal assignment of the absorption spectrum of the first singlet excited state of the *N*,*N*-dialkylanilino chromophore in 4-cyclohexyl-*N*,*N*-dimethylaniline (**1**), **2**, 1-phenyl-4-cyclohexylpiperidine (**3**) and **4**. It has a maximum positioned between 600 and 635 nm.

Introduction

The *N*,*N*-dialkylanilino chromophore has been widely applied as electron donor in photoinduced electron-transfer studies.[1] In connection with this, and also for other reasons, the photophysical properties of the chromophore have been the subject of numerous investigations. Among these are studies[2] on the ground-state UV absorption,[3−7] fluorescence,[8,9] triplet absorption,[10−14] phosphorescence,[8,15−17] and excited-state dipole moments.[18−20] Despite all these studies, the excited state properties of the dialkylanilino chromophore have not yet been completely disclosed.

Our interest in some aspects of the photophysics of the *N*,*N*-dialkylanilino chromophore was raised when studying photoinduced charge separation in donor−bridge−acceptor compounds **DA1** and **DA2** (Chart 1), in which the *N*,*N*-dialkylanilino chromophore and the central olefinic bond in **DA2** act as electron donors, while the dicyanoethylene moiety acts as an electron acceptor.[21] It was found that the presence of the central olefinic bond in **DA2** considerably reduces the fluorescence lifetime τ_f of the (conformationally extended) charge transfer state [D$^{+\bullet}$−bridge−A$^{-\bullet}$]* as compared to **DA1** ($\tau_f = 2$ ns vs 36 ns in benzene). The olefinic bond also had a profound influence on the excited-state properties of 1-phenyl-4-cyclohexylpiperidine (**3**) and 1-phenyl-4-cyclohexylidenepiperidine (**4**), which lack the dicyanoethylene acceptor. Whereas for **3** transient absorption (TA) spectroscopy revealed a long-lived triplet absorption at 475 nm, which is usual for *N*,*N*-dialkylanilines, in the case of **4** this absorption was virtually absent, suggesting that the triplet state of **4** is effectively quenched, presumably due to the presence of the olefinic bond.[21] Only a short-lived (τ < 5 ns) broad absorption band positioned at 635 nm was observed, which was tentatively interpreted to originate from the S$_1$ state of the *N*,*N*-dialkylanilino chromophore. In the TA spectra of **3** a shoulder in the same wavelength region was detectable at short delay times. Observation of the *N*,*N*-dialkylanilino S$_n$ ← S$_1$ absorption has thus far not been reported.

CHART 1



Here we present evidence that the 635 nm absorption observed for **4** is indeed derived from the S$_1$ state of the *N*,*N*-dialkylanilino chromophore as provided by a study of the photophysical properties of two structurally related compounds, 4-cyclohexyl-*N*,*N*-dimethylaniline (**1**) and 4-(4-(propan-2-ylidene)cyclohexyl)-*N*,*N*-dimethylaniline (**2**). These compounds consist of an *N*,*N*-dialkylanilino donor substituted at its *para*-position by a cyclohexane ring, to which in the case of **2** an isopropylidene group is attached (see Chart 1). As a consequence, the spatial separation between the olefinic bond and the *N*,*N*-dialkylanilino group in **2** is enlarged by a single σ-bond in comparison to **4**. The detailed study of the photophysical properties of **1**−**4** provides unambiguous evidence that the observation of only the S$_1$ absorption spectrum in the case of **4** is due to efficient triplet−triplet quenching.

The results presented here provide insight in the excited-state properties of the important *N*,*N*-dialkylanilino chromophore.

Results and Discussion

Absorption Spectroscopy. To investigate whether any ground-state electronic interaction between the olefinic bond

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10.1021/jp0044983 CCC: $20.00

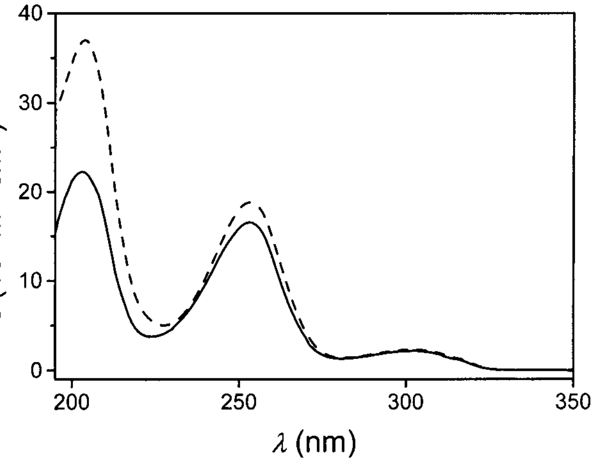


Figure 1. Absorption spectra of **1** (—) and **2** (- - -) in cyclohexane at 20 °C in the range 195−350 nm.

TABLE 1: Absorption Maxima λ_{max} and Molar Absorption Coefficients ε of Compounds 1−6 in Cyclohexane at 20 °C

compound	λ_{max} (nm) [ε(10^3 M^{-1} cm^{-1})]		
1	203.5 [22.5 ± 0.5]	253.5 [16.54 ± 0.16]	302.0 [2.28 ± 0.03]
2	204.0 [35.5 ± 0.9]	253.0 [18.80 ± 0.16]	302.5 [2.31 ± 0.03]
5[42]		251.3 [14.9]	297.6 [2.3]
3[21]	203 [18.1]	255 [13.3]	289 [1.6]
4[21]	210 [22.9]	255 [15.5]	289 [1.8]
6[4] [a]		254.0 [12.00 ± 0.24]	287[b] [1.58 ± 0.03]

[a] Solvent 2,2,4-trimethylpentane. [b] Broad shoulder.

and the *N*,*N*-dialkylanilino chromophore occurs, the absorption spectra of **1** and **2** were examined. They are presented in Figure 1 while absorption maxima (λ_{max}) and molar absorption coefficients (ε) are given in Table 1.

Compound **1** shows absorption bands with λ_{max} values of 203.5, 253.5, and 302.0 nm in cyclohexane. The last two bands, which are typical for *N*,*N*-dialkylanilines, represent the ^1L_a and the ^1L_b transitions, respectively.[6] In the absorption spectrum of **2**, the 203.5 nm *N*,*N*-dialkylanilino band overlaps with the $\pi^* \leftarrow \pi$ transition of the olefinic bond, which for bicyclohexylidene (**7**) is positioned at 206 nm in *n*-pentane ($\varepsilon \sim 11 \times 10^3$ M^{-1} cm^{-1}).[22,23] Since neither additional bands nor band shifts are observed for **2** as compared to **1**, it is inferred that the electronic interaction between the two chromophores in **2**, if present, is small. The results for **1** and **2** are in line with those previously reported for **3** and **4**.[21]

Nevertheless, there is a small but distinct increase in absorption intensity of the ^1L_a band in both **2** and **4** relative to their reference compounds **1** and **3**. This cannot be explained by a superposition of bands, since the absorption onset of the olefinic chromophore in bicyclohexylidene (**7**) is 230 nm.[23] It may, however, be attributed to intensity borrowing from the $\pi^* \leftarrow \pi$ transition of the olefinic bond by the anilino ^1L_a transition. It is known that the polarization of the ^1L_a transition of *N*,*N*-dimethylaniline (**5**) has mixed *x* and *z* character,[16,17] while the $\pi^* \leftarrow \pi$ transition of **7** is polarized along the *z* axis,[23−26] providing a favorable orientation of transition dipole moments for intensity borrowing to occur.

TABLE 2: Time-Resolved and Steady State Fluorescence Data of 1−4

	solvent	$\lambda_{max,f}$ (nm)	τ_f (ns)	Φ_f
1	cyclohexane	335	2.33	0.16
	benzene	343	2.70	0.14
	diethyl ether	340	3.29	0.18
2	cyclohexane	334	2.39	0.12
	benzene	343	2.81	0.13
	diethyl ether	339	3.40	0.15
3[43]	cyclohexane	336	1.7	0.25
	benzene	343	2.5	0.35
4[43]	cyclohexane	336	2.0	0.25
	benzene	343	2.3	0.34

TABLE 3: TRMC Results for 1 and 2[a]

compound	solvent	T_1, τ (μs)	S_1, μ_{cyl}	S_1, μ_{sph}	$\phi_{isc}(\mu_T/\mu_S)^2$
1	cyclohexane	>1	9.3	7.3	0.09
	benzene	>1	6.3	4.8	0.13
2	cyclohexane	0.16	10.8	7.7	0.10
	benzene	0.21	6.6	4.6	0.16

[a] Dipole moments (in debye) of the S_1 state are given assuming a cylindrical and a spherical geometry.

Emission Properties. The steady-state fluorescence maxima ($\lambda_{max,f}$) and fluorescence quantum yields (Φ_f) of **1** and **2** together with fluorescence lifetimes (τ_f) obtained by the single photon counting (SPC) technique in three solvents are presented in Table 2. Excellent monoexponential decay fits were obtained in all cases. The results show that the presence of an olefinic bond in **2** and **4** does not have an appreciable effect on $\lambda_{max,f}$, τ_f, as well as Φ_f values. Even the solvent dependence of these parameters does not differ from those of the reference compounds **1** and **3**. Hence, upon going from **1** to **2** and from **3** to **4**,[21] the properties of the lowest excited singlet (S_1) state, which is localized on the *N*,*N*-dialkylanilino chromophore, are not affected by incorporation of the olefinic bond. Consequently, any difference in excited state behavior upon the incorporation of the olefinic bond can only stem from states other than the S_1 state.

Time-Resolved Microwave Conductivity. Time-resolved microwave conductivity[27] (TRMC) transients of **1** and **2** were obtained in cyclohexane and benzene upon excitation at 308 nm. The transients measured in benzene are presented in Figure 2. They both show the contribution of the short-lived S_1 state at early times and the T_1 triplet state at longer times. The transients were fitted with the singlet lifetimes fixed at the SPC values (Table 2). The resulting T_1 lifetimes τ, as well as the S_1 state dipole moments for cylindrical (μ_{cyl}) and spherical (μ_{sph}) geometries and the quantity $\phi_{isc}(\mu_T/\mu_S)^2$, in which μ_S and μ_T represent the dipole moments of the S_1 state and the T_1 state, respectively, and ϕ_{isc} is the quantum yield for intersystem crossing, are collected in Table 3. From the transients it is clear that the triplet lifetime of **1** is much longer than that of **2**. Rather short triplet lifetimes of 160 ± 30 ns and 210 ± 20 ns were obtained for **2** in cyclohexane and benzene, respectively, which agree very well with the lifetimes obtained by TA (see next section). For 1 it was not possible to determine reliable triplet lifetimes, since they were too long (in the microsecond range) for the time window of the experimental setup.

An interesting parameter is the quantity $\phi_{isc}(\mu_S/\mu_T)^2$. In both cyclohexane and benzene the values of $\phi_{isc}(\mu_S/\mu_T)^2$ for **1** and **2** are of similar magnitude. If the ratio μ_S/μ_T is equal for **1** and **2**, this implies that the presence of an olefinic bond does not affect the quantum yield of triplet formation. As is evident from the values in Table 3, the S_1 dipole moments of **1** and **2** are almost equal in a given solvent. Although quantitative information on the dipole moments of the triplet states for **1** and **2** is not available, it is expected that the magnitude of their triplet dipole moments should be similar due to the fact that their triplet states are both localized on the *N*,*N*-dialkylanilino moiety (see next section). This is corroborated by the very similar magnitudes of the TRMC transients in the first 50 ns. Thus, the TRMC

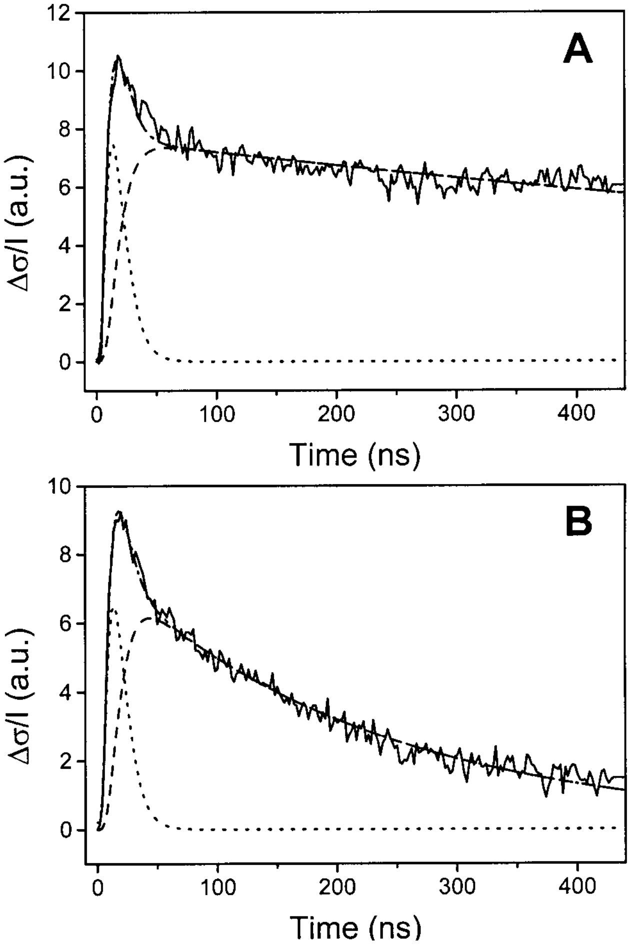


Figure 2. Time-resolved microwave conductivity transients of **1** (A) and **2** (B) in benzene. Apart from the measured signal (solid line), the contributions of the singlet (dotted line) and the triplet (dashed line) component to the fit (dash−dot) are shown.

TABLE 4: Transient Absorption Data of 1 and 2

compound	solvent	T_1, λ_{max} (nm)	T_1, τ (μs)	S_1, λ_{max} (nm)[a]	S_1, τ (ns)[b]
1	cyclohexane	350 ± 10; 459 ± 4	2.1	624	2.8
	benzene	355 ± 20; 468 ± 4	2.0	602	3.1
	diethyl ether	353 ± 5; 460 ± 2	1.2	614	2.5
2	cyclohexane	346 ± 5; 460 ± 2	0.160	623	2.5
	benzene	341 ± 10; 465 ± 4	0.225	610	2.4
	diethyl ether	353 ± 4; 461 ± 2	0.180	613	2.6

[a] Estimated error in peak position: 10 nm. [b] Estimated error: 0.3 ns.

results indicate that the triplet state is formed in equal amounts in both **1** and **2**. The decay of the *N*,*N*-dialkylanilino triplet state is however dramatically enhanced by the incorporation of the olefinic bond.

Transient Absorption Spectroscopy. Nanosecond TA spectroscopy was performed on **1** and **2** in three solvents. Typical TA traces of **1**−**4** are presented in Figure 3; lifetimes (τ) and absorption maxima (λ_{max}) of **1** and **2** are reported in Table 4. According to the analysis of the TA spectra, in all cases two species were observed. Whereas one species is short-lived (τ 2.1−3.4 ns) and has a λ_{max} positioned at 602−624 nm, the other species is characterized by a fast rise time and a long decay time (τ 0.160−2.1 μs) and has absorption maxima at 341−355 nm (not shown) and 459−468 nm. The latter species can be readily associated with the triplet state (T_1) absorption spectrum of *N*,*N*-dialkylanilines.[14]

Singlet Excited State Absorption of *N*,*N*-Dialkylanilines. The TA lifetimes of the short-lived species agree well with the fluorescence lifetimes (see Table 2). A short-lived (τ < 5 ns) absorption in the range 625−635 nm was also observed for **3** and **4** in benzene.[21] Hence in all solvents, for **1**−**4** a transient absorption band is found in the wavelength range 600−635 nm, of which the lifetime is very similar to the fluorescence lifetime. Therefore, it is concluded that this absorption stems from the S_1 state of the *N*,*N*-dialkylanilino chromophore.

Further support for the nature of the 600−635 nm band was obtained by TA measurements of **3** in benzene with a streak camera. By means of principle component analysis using singular value decomposition of the streak camera image, the absorption spectra of the individual species and their time dependent concentration profiles were obtained.[28,29] As can be seen from the concentration profiles presented in Figure 4A, the formation of the triplet absorption (τ = 3.3 ns) is coupled to the decay of the 600 nm absorption (τ = 3.2 ns). The associated spectra are shown in Figure 4B. While the spectrum of the S_1 state has a single maximum at 600 nm in the observed range (440−750 nm), that of the triplet state has a maximum at 470 nm. Note that the calculated concentration profiles bear a large resemblance to the TRMC transients.

To our knowledge, the detection of an S_1 absorption of *N*,*N*-dialkylanilines in the wavelength region 440−750 nm has not yet been reported. Until now only one proposal for the S_1 absorption spectrum of **5** is available in the literature.[13] From a pulse radiolysis and flash photolysis study of **5** in the wavelength range 375−1600 nm it was tentatively concluded that its S_1 spectrum exhibits a broad and weak absorption band in the region 700 to >1600 nm; no broad band near 600 nm was found. In view of our results this proposal now appears to be incorrect. It is somewhat remarkable that a proper spectrum of the S_1 state of the frequently employed *N*,*N*-dialkylanilino chromophore has never been reported. There are however several reasons which provide an explanation for this: (1) unfavorable experimental conditions, such as an insufficient time resolution of the experimental setup; (2) A large overlap of singlet and triplet absorption spectra, which prevents the S_1 spectrum from being discerned (for example, compare Figures 3C and 4B); (3) The occurrence of rapid deactivating processes such as singlet excited-state energy transfer to chromophores with lower excitation energy or electron transfer to an electron acceptor; and (4) usually, lower energy chromophores than the anilino group are excited. This is done either because of experimental convenience or in order to avoid energy transfer processes as mentioned under 3.

Triplet−Triplet Energy Transfer. The long-lived transient absorption of **1** and **2**, with band maxima at 341−355 nm (not shown in Figure 3) and 459−468 nm, is typical for the triplet state of *N*,*N*-dialkylanilines.[14] It was also observed for **3**, but was absent in the TA spectrum of **4**.[21] When comparing the lifetimes of the triplet absorption of **1** and **2** it is striking that those of **2** are shorter by a factor of 10. Hence, the presence of an olefinic bond in **2** also leads to quenching of the triplet state. Interestingly, the effect is however much less pronounced. In **4** the decay around 475 nm, where the triplet absorption band is expected, is slower than at 635 nm, where the S_1 state absorbs (Figure 3D). This shows that in **4** also the aniline triplet state is populated, but that it decays with a lifetime on the order of 10 ns, which is a factor of about 20 faster than in **2** (see Table 4). This is consistent with a quenching process that is very strongly distance-dependent, which is typical for energy transfer via an electron exchange mechanism.[30] Since triplet−triplet energy

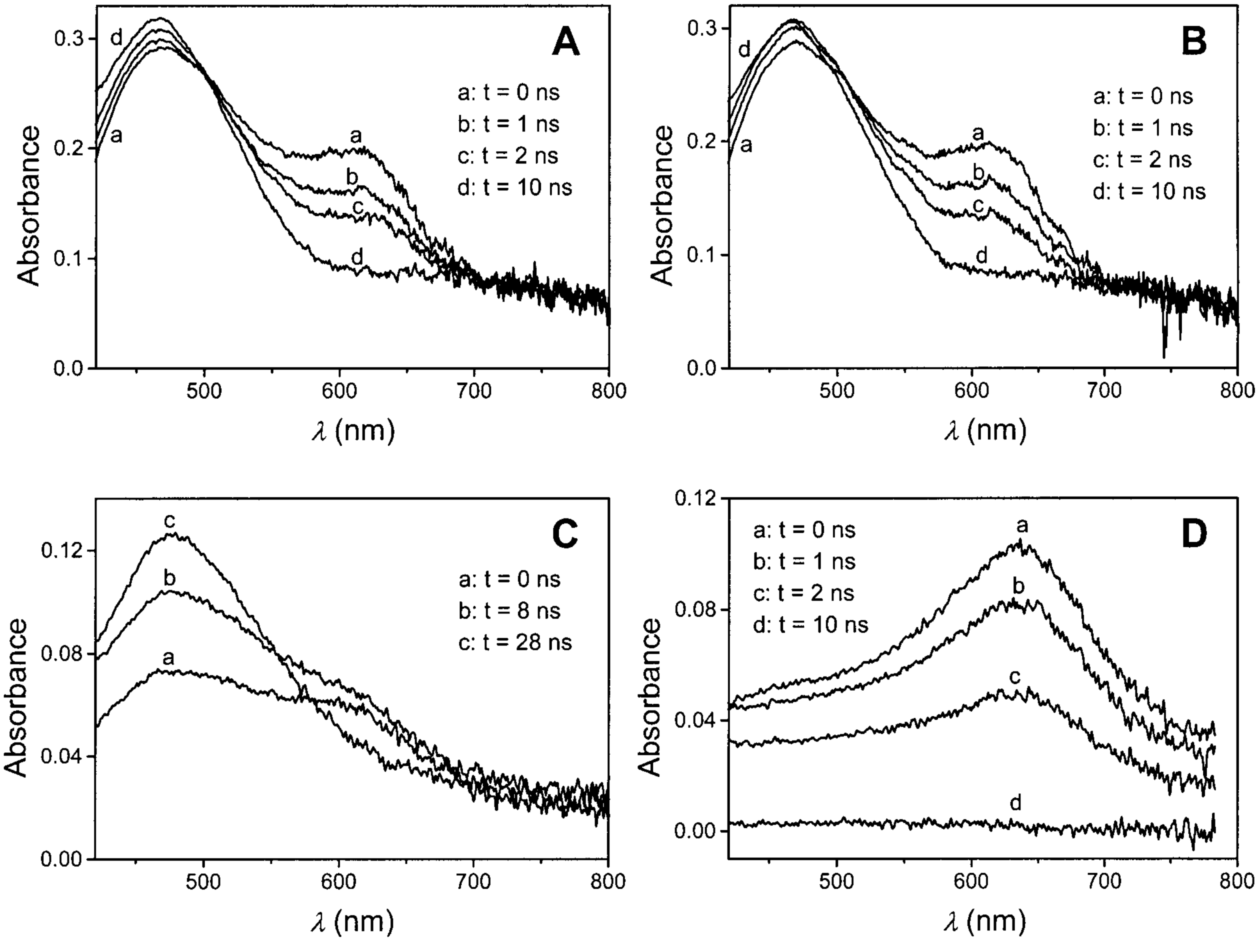


Figure 3. Transient absorption spectra of **1** (A) and **2** (B) in diethyl ether in the range 420−800 nm. The spectra at $t = 0$ ns are recorded at the maximum of the excitation pulse. A cutoff filter (<420 nm) was used. For comparison transient absorption spectra of **3** (C) and **4** (D) in benzene in the same wavelength range[21] are given as well.

transfer has to occur via the electron exchange mechanism, this is the most probable quenching process. The obvious triplet energy acceptor is the olefinic bond. Further support is given by the triplet energies of *N*,*N*-dimethylaniline and bicyclohexylidene which are ca. 3.5 eV[15] and ca. 3.3 eV,[22] respectively. Once populated, the triplet state of the olefinic bond is forced to attain a twisted conformation which will deactivate rapidly by crossing to the S_0 ground state.[30] Even a very fast triplet−triplet energy transfer decay channel is not expected to influence the singlet excited state lifetime considerably if the kinetic scheme in Scheme 1 applies. This is in accordance with the observed insensitivity of the singlet lifetimes to the presence of the olefinic bond.

It is possible that the strong distance dependence of the triplet energy transfer process is governed by the presence of conformers[31] in which there is either a very small separation between the chromophores or a favorable orientation for through-bond interaction.[32,33] Therefore, the conformational properties of **1**−**4** were assessed with ^{1}H NMR spectroscopy and calculations at the B3LYP/6-31G level of theory. As judged from the tt-like coupling pattern of the methine ^{1}H NMR resonances centered at δ 2.39 (**1**) and δ 2.59 (**2**) ppm, respectively, which is typical for a proton in an axial position, the anilino group in both **1** and **2** occupies—as expected—an equatorial position.[34] Furthermore, from the presence of distinct ^{1}H NMR resonances for axial and equatorial positioned methylene protons in **2** it can be deduced that the equatorial position of the anilino group locks the cyclohexyl ring in a single chair conformation on the NMR time scale. Conformational uniformity of the saturated rings was also established for **3**.[21] Here the equatorial orientation of the cyclohexyl substituent locks the piperidino ring in a single chair conformation (and vice versa), while the *N*-phenyl group occupies a (pseudo) equatorial position.[21] ^{1}H NMR indicates that in **4** the incorporation of a double bond allows it to interconvert between two or two sets of degenerate conformers which are interrelated by coupled chair−chair interconversion and nitrogen inversion of the piperidino ring.[21] Since this process is rapid on the NMR time scale, NMR does not give much information about the actual geometry. Therefore, calculations at the B3LYP/6-31G level of theory were done on various conformers of **4**, viz., **4** (equatorial, eq), with the phenyl group in an equatorial position and the piperidino ring in a chair conformation, **4** (axial, ax) with the phenyl group in an axial position and the piperidino ring in a chair conformation and **4** (twist boat) with the piperidino ring in a twist boat conformation,[35] respectively. A comparison of their energies shows only moderate differences. The lowest energy was found for **4** (eq), while **4** (ax) and **4** (twist boat) are 0.79 and 0.70 kcal/mol higher in energy, respectively. Consequently, several conformers are accessible for **4**. However, for all conformers, the through-space distance between the anilino and alkene chromophores is similar. Taking the closest atom-to-atom distance, this distance amounts to 2.9−3.0 Å. For **2**, the anilino-alkene separation in the B3LYP/6-31G optimized geometry is 4.4 Å. Thus, in both **2** and **4** not only the through-bond distance (four and three bonds respectively) but also the through-space distance between the anilino and alkene chromophores appears to be well-defined in the ground state.

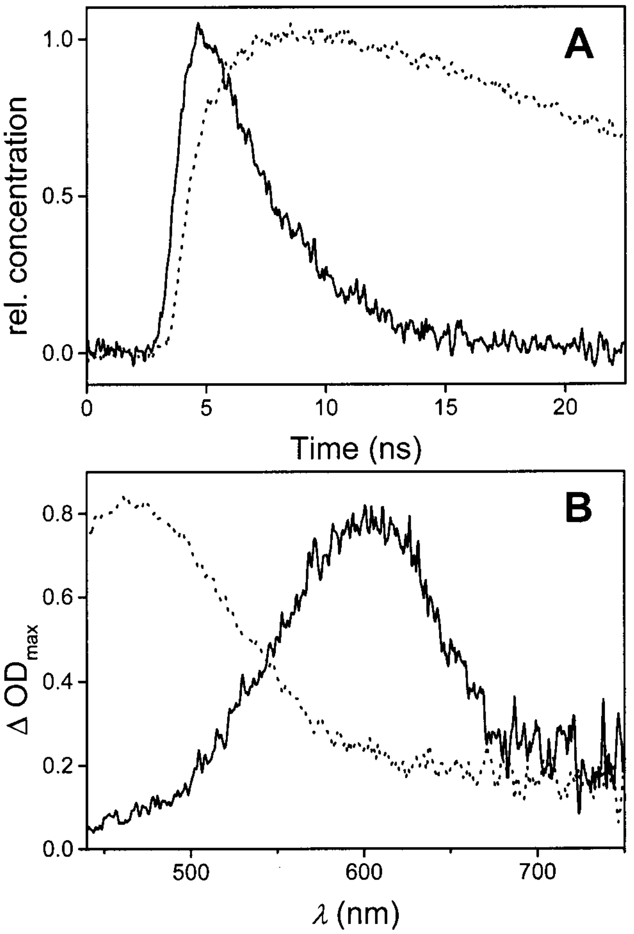
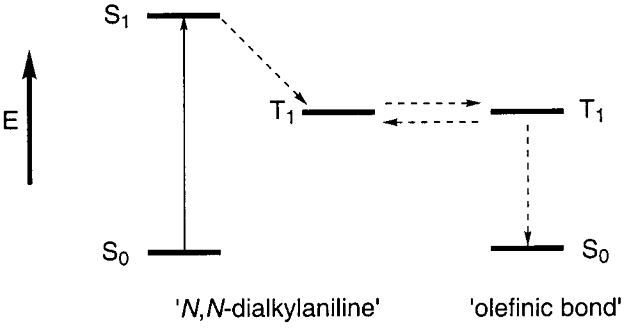


Figure 4. Time dependent relative concentration profiles of the excited singlet (—) and triplet state (···) of **3** in benzene as reconstructed from the streak image by singular value decomposition (A) and the corresponding absorption spectra in the range 440−750 nm (B). Excitation wavelength: 300 nm. Note that this sample was not purged with Ar.

SCHEME 1: Schematic State Diagram for Triplet−Triplet Energy Transfer for 2 and 4



In a series of donor-bridge-acceptor systems containing bridges related to those employed here, it has been established by Closs et al.[36] that triplet energy transfer occurs dominantly by a through-bond mechanism unless D and A are in very close proximity. Thus, also in our systems it is likely that a through-bond mechanism prevails. The rate of energy transfer via electron exchange k_{EET} is expected to be subject to an exponential dependence on the distance as expressed in the number of intervening bonds n: $k_{EET} \sim \exp(-\alpha n)$. Employing a typical damping factor of $\alpha = 2.6$ per bond,[36] it is predicted that (all others being equal) energy transfer in **4** should be faster than in **2** by a factor of 13.5. This is of the same order of magnitude as the observed ratio $k_{EET}(\mathbf{4})/k_{EET}(\mathbf{2}) = 20$. The most important reason for the actual ratio being somewhat larger than predicted may be the difference in the way the anilino chromophore is oriented. In **4** the nitrogen atom is directly connected to two parallel 3σ bond pathways leading to the double bond. In **2** the connection is by a single bond that allows rotational freedom diminishing through-bond interaction.[37]

Conclusions

The olefinic bond in compounds **2** and **4** hardly influences the ground and singlet excited-state properties of the *N*,*N*-dialkylanilino chromophore. The TRMC results indicate that the quantum yield of triplet formation is also independent of the presence of a double bond. In **2** and **4**, however, the *N*,*N*-dialkylanilino T_1 state is quenched by the olefinic bond via triplet−triplet energy transfer. This quenching process is much faster in **4** than in **2** due to the shorter distance (less σ-bonds) between the chromophores in **4**. Furthermore, it was shown that the short-lived 600−635 nm transient absorption band in compounds **1**−**4** stems from the S_1 state of the *N*,*N*-dialkylanilino chromophore.

Experimental Section

General. ^{1}H NMR spectra were recorded at 300 K using a Bruker AC300 NMR spectrometer operating at 300.133 MHz. Chemical shifts are given relative to internal TMS. Spectroscopic grade solvents were used throughout in the photophysical measurements.

Synthesis of Compounds 1−4. The synthesis of **3** and **4** has been reported previously.[21] Whereas compound **1** was prepared by catalytic hydrogenation of 4-cyclohex-1-enyl-*N*,*N*-dimethylaniline, compound **2** was synthesized by decarboxylative dehydration of a β-hydroxy acid obtained by coupling of 4-(4-(*N*,*N*-dimethylamino)phenyl)cyclohexanone and isobutyric acid using procedures described in ref 38. For **1** and **2** satisfactory analytical data were obtained; details will be published elsewhere.

Steady State Absorption and Fluorescence Spectroscopy. UV−vis absorption spectra were recorded on either a Cary 1 or a Cary 5 spectrophotometer (Varian) operating with 0.5 nm spectral resolution. Peak positions are given with 0.5 nm accuracy. Steady-state fluorescence measurements were carried out on a Spex Fluorolog-2 spectrofluorometer consisting of a 150 W high-pressure ozone-generating Xe arc lamp excitation source, a Spex 1680 0.22m double spectrometer as the excitation monochromator, a Spex 1681 0.22m spectrometer as the emission monochromator, and a Hamamatsu R928 photomultiplier tube as detection system. Emission and excitation spectra were corrected for the wavelength-dependent response of the detection system with the aid of correction files provided by the manufacturer. Fluorescence quantum yields were determined relative to naphthalene in cyclohexane ($\phi = 0.23 \pm 0.02$[39]) at 20 °C (excitation at 285 nm). Solutions were purged with Ar for at least 10 min prior to measurement. Corrections for solvent refractive indices were made according to Eaton[39] when needed.

Time-Resolved Measurements. The experimental details for time-resolved microwave conductivity measurements were the same as described in ref 21. An absorbance of 1 cm^{-1} at the excitation wavelength was chosen. No evidence of solute aggregation was found. Up to 60 transients were averaged to enhance the signal-to-noise ratio.

For the measurement of transient absorption spectra a Coherent Infinity-XPO laser with SHG option was used as the excitation source, delivering 2 ns, 3 mJ pulses in the wavelength range 220−340 nm. The excitation wavelength was chosen to be close to the absorption maximum around 300 nm of the sample studied. Typical absorbance of the samples was 1−2 cm^{-1} at the excitation wavelength. A pulsed low pressure Xe lamp (5 J maximum energy at 10 Hz pulse repetition rate) was used as probe light in a right angle geometry. The probe light was collected on a Princeton Instruments time gated (5 ns) intensified CCD camera after passing through a spectrograph, covering a spectral range of 600 nm. The detector was gated at 5 ns. Typically 25 spectra were averaged to obtain a satisfactory signal-to-noise ratio.

Picosecond single photon counting (SPC) fluorescence decay was measured using the setup and computer programs described in ref 40. The samples were degassed by purging with Ar for 10 to 15 min and were excited at 310−320 nm.

Calculations. The geometries of the various conformers of **4** were optimized without any geometrical constraints at the B3LYP/6-31G level of theory using GAMESS−UK.[41] The obtained total energies (in hartree) and, between parentheses, the closest atom-to-atom distances (in angstroms) as defined in the text are (**2**) −717.433160, (**4**, eq) −716.225851 (2.90), (**4**, ax) −716.224590 (2.96), (**4**, twist boat) −716.224738 (2.98) (see also Supporting Information).

Acknowledgment. This research has been financially supported (W.D.O. and M.K.) by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO).

Supporting Information Available: Cartesian coordinates and structure drawings of the B3LYP/6-31G optimized geometries of **2**, **4** (eq), **4** (ax,) and **4** (twist boat). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(2) Padma, E. J.; Jug, K. *J. Phys. Chem.* **1984**, *88*, 3508.

(3) Klevens, H. B.; Platt, J. R. *J. Am. Chem. Soc.* **1949**, *71*, 1741.

(4) Bottini, A. T.; Nash, C. P. *J. Am. Chem. Soc.* **1962**, *84*, 734.

(5) Kimura, K.; Tsubomura, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1336.

(6) Ballester, M.; Riera, J. *Spectrochim. Acta, Part A* **1967**, *23*, 1533.

(7) Dubroca, C. *Chem. Phys. Lett.* **1972**, *15*, 207.

(8) Davidson, R. S.; Santhanam, M. *J. Chem. Soc. B* **1971**, 1151.

(9) Köhler, G. *J. Photochemistry* **1987**, *38*, 217.

(10) Kimamura, K.; Arimitsu, S.; Yamamoto, N.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1274.

(11) Kimura, K. *Mol. Phys.* **1968**, *15*, 109.

(12) Cadogan, K. D.; Albrecht, A. C. *J. Phys. Chem.* **1969**, *73*, 1868.

(13) Land, E. J.; Richards, J. T.; Thomas, J. K. *J. Phys. Chem.* **1972**, *76*, 3805.

(14) Previtali, C. M. *J. Photochem.* **1985**, *31*, 233.

(15) Kimura, K.; Tsubomura, H. *Mol. Phys.* **1966**, *11*, 349.

(16) Lim, E. C.; Chakrabarti, S. K. *J. Chem. Phys.* **1967**, *47*, 4726.

(17) Lim, E. C.; Chakrabarti, S. K. *Chem. Phys. Lett.* **1967**, *1*, 28.

(18) Prabhumirashi, L. S.; Kutty, D. K. N.; Bhide, A. S. *Spectrochim. Acta, Part A* **1983**, *39*, 663.

(19) Weisenborn, P. C. M.; Varma, C. A. G. O.; de Haas, M. P.; Warman, J. M. *Chem. Phys.* **1988**, *122*, 147.

(20) Shimamori, H.; Sato, A. *J. Phys. Chem.* **1994**, *98*, 13481.

(21) Hoogesteger, F. J.; van Walree, C. A.; Jenneskens, L. W.; Roest, M. R.; Verhoeven, J. W.; Schuddeboom, W.; Piet, J. J.; Warman, J. M. *Chem. Eur. J.* **2000**, *6*, 2948.

(22) Allan, M.; Snyder, P. A.; Robin, M. B. *J. Phys. Chem.* **1985**, *89*, 4900.

(23) Hoogesteger, F. J.; van Lenthe, J. H.; Jenneskens, L. W. *Chem. Phys. Lett.* **1996**, *259*, 178.

(24) Havenith, R. W. A.; van Lenthe, J. H.; Jenneskens, L. W.; Hoogesteger, F. *J. Chem. Phys*. **1997**, *225*, 139.

(25) Snyder, P. A.; Clark, L. B. *J. Chem. Phys.* **1970**, *52*, 998.

(26) Yogev, A.; Sagiv, J.; Mazur, Y. *J. Am. Chem. Soc.* **1972**, *94*, 5122.

(27) de Haas, M. P.; Warman, J. M. *Chem. Phys.* **1982**, *73*, 35.

(28) Koeberg, M.; Werts, M. H. V.; van Ramesdonk, H. J.; Verhoeven, J. W. *Hamamatsu News* **2000**, *2*, 16.

(29) Werts, M. H. V. Luminescent Lanthanide Complexes. Ph.D. Thesis, University of Amsterdam, Amsterdam, The Netherlands, 2000.

(30) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, 1978.

(31) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237.

(32) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

(33) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(34) (**1**) ^{1}H NMR ($CDCl_3$) δ 1.16−1.45 (m, 5H), 1.69−1.87 (m, 5H), 2.35−2.44 (m, 1H), 2.89 (s, 6H), 6.67−6.72 (AA′BB′ system, 2H), 7.06−7.11 (AA′BB′ system, 2H). The multiplet of **1** centered at 2.39 ppm has a tt-like multiplicity, but is not well resolved, presumably due to the presence of multiple conformations of the cyclohexane-ring. (**2**) ^{1}H NMR ($CDCl_3$) δ 1.34−1.48 (m, 2H), 1.69 (t-like, 6H, $J = 1.4$ Hz), 1.82−1.97 (m, 4H), 2.59 (tt-like, 1H, $J = 12$ Hz and $J = 3.4$ Hz), 2.75−2.80 (m, 2H), 2.89 (s, 6H), 6.67−6.72 (m, 2H), 7.06−7.11(m, 2H).

(35) Note that in the twist boat conformation the phenyl group occupies a fixed position since the nitrogen atom is sp^2 hybridized (the sum of the bond angles around N is 360.00°).

(36) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652.

(37) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

(38) Hoogesteger, F. J.; Havenith, R. W. A.; Zwikker, J. W.; Jenneskens, L. W.; Kooijman, H.; Veldman, N.; Spek, A. L. *J. Org. Chem.* **1995**, *60*, 4375.

(39) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.

(40) Willemse, R. J.; Piet, J. J.; Warman, J. M.; Hartl, F.; Verhoeven, J. W.; Brouwer, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 3721.

(41) GAMESS−UK is a package of ab initio programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, P. Sherwood and, R. J. Harrison with contributions from, R. D. Amos, R. J. Buenker, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, V. R. Saunders, and A. J. Stone. The package is derived from original GAMESS code due to M. Depuis, D. Spangler, and J. Wendolowski, NRCC Software Catalog, Vol. 1; Program No. QG01 (GAMESS), 1980.

(42) van Walree, C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.

(43) Hoogesteger, F. J. Oligo(Cyclohexylidenes), Development of Novel Functional and Organized Materials. Ph.D. Thesis, Utrecht University, Utrecht, The Netherlands, 1996.