Effect of the Nitrogen Heteroatom on the Excited State Properties of 1,4-Distyrylbenzene

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The photophysical and photochemical properties of some aza-analogues of 1,4-distyrylbenzene, bearing a nitrogen heteroatom in the side arene rings, have been investigated. The kinetic competition between the radiative and reactive relaxation channels of the lowest excited singlet state has been compared with that of the parent hydrocarbon. The replacement of the side phenyl rings with pyridyl or quinolyl rings was found to markedly affect the photobehavior of the three stereoisomers (*EE*, *ZE*, and *ZZ*). Adiabatic formation of the excited $^1EE^*$ by irradiation of the other isomers was evidenced by fluorescence measurements. The effect of the presence of the heteroatom in the central ring, while maintaining the linear conjugation, was investigated for *EE*-2,5-distyrylpyridine, and it was found to be less important than that of N in the side rings. Information about the conformational equilibria of the compounds bearing side quinolyl groups or the pyridyl central ring, due to internal rotation around the quasi single bonds with the ethenic carbons, was obtained by selective photoexcitation.

Introduction

The photobehavior of distyrylbenzenes and analogous compounds in which a central arene group is substituted by arylethenyl moieties has been extensively investigated in the last 2 decades because of their interest as laser dyes, scintillators, and building blocks of polyphenylenevinylene materials having potential applications in optoelectronics.[1,2]

The parent hydrocarbon, distyrylbenzene, $(St)_2B$, exists in three different structures depending on whether the two styryl substituents are in the para (1,4), meta (1,3) or ortho (1,2) positions of the central benzene ring. The 1,4 (linear conjugation) and 1,3 (crossed conjugation) compounds have been extensively investigated;[1,3−10] both have a very low photoisomerization yield. The 1,4 compound is spectroscopically similar to stilbene, but in contrast to the latter, the radiative relaxation pathway prevails over the reactive one. The first absorption band corresponds to an allowed $A_g \rightarrow B_u$ electronic transition, the emitting state being the same as that reached by absorption. The 1,3 compound is characterized by a first weak transition to a forbidden state; the emission, which has a longer lifetime, remains largely prevalent over the reactive pathway. Moreover, this isomer exists as a mixture of at least two rotamers which differ in their photophysical and photochemical properties and can be revealed by fluorimetry.[1]

Introducting heteroatoms into these hydrocarbons, e.g., by replacing the side phenyl groups with pyridyl or quinolyl groups, may markedly affect their excited state properties. Our laboratory has extensively investigated the effect of nitrogen heteroatoms on the photophysics and photochemistry of stilbenelike molecules for some series of diarylethenes[11−16] and diarylbutadienes.[17,18] Our interest in distyrylbenzene aza-analogues started with a study of the photobehavior of some pyridine derivatives, 2,6-disubstituted with arylethenyl groups.[19]

The aim of the present work was to study the photophysical and photochemical properties of some analogues of the symmetrically substituted 1,4-$(St)_2B$, of general formula $(Ar-CH=CH-)_2B$, bearing a nitrogen heteroatom in the side arene rings. Since the abundant literature data on $(St)_2B$ (most of which are nicely described in a 1992 review article[1]) are scattered or refer to compounds that are alkyl-substituted at the side aryl groups, the parent hydrocarbon was also revisited in the present work in order to get more comparable information on the unsubstituted compound using the same experimental conditions.

The kinetic competition between the radiative and reactive relaxation channels of the lowest excited singlet state of three nitrogen-containing isomers of 1,4-$(St)_2B$ is here described and compared with that of the parent hydrocarbon. The excited-state properties of the three stereoisomers (*EE*, *ZE*, and *ZZ*) were investigated. Adiabatic formation of the excited $^1EE^*$ by irradiation of the other isomers was evidenced by fluorescence measurements.

The effect of the heteroatom in the central ring on the photobehavior, already reported for the cross-conjugated 2,6-distyrylpyridine,[19] was now investigated for the isomeric 2,5-distyrylpyridine, which maintains a linear conjugation, and found to be less important than that of nitrogen in the side rings.

Experimental Section

Materials and Experimental Measurements. The compounds investigated (Chart 1) were prepared at the Padua laboratory by application of a 2-fold Wittig reaction to difunctional reactants. Both syntheses, from benzyltriphenyl-phosphonium bromide and terephthalic aldeyde, and/or from *p*-xylylene-bis(triphenylphosphonium bromide) and benzaldehyde, were used for the hydrocarbon and, by appropriately changing the reagents, for the aza-derivatives. The products obtained were characterized by one- and two-dimensional ^1H NMR spectra using a Bruker AC 400 spectrometer and TMS as reference (see Table S1, Supporting Information). The solvents used were 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP), ben-

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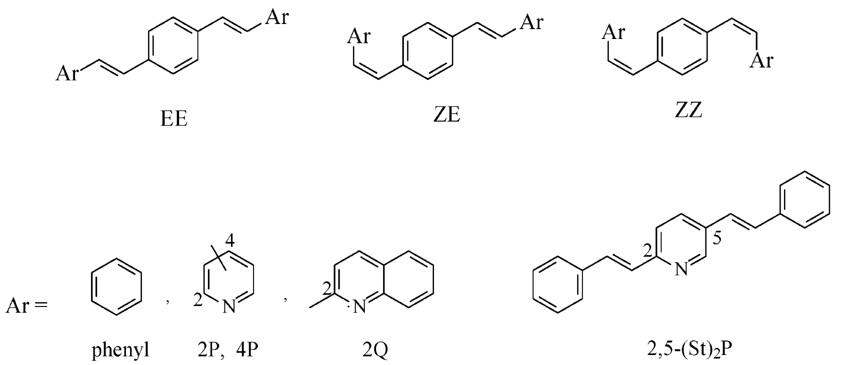
CHART 1



zene, and toluene; for NMR analyses, deuterated benzene and dimethyl sulfoxide (DMSO) were used. Some optical measurements at liquid nitrogen temperature were also carried out in 5/5/2 diethyl ether/isopentane/ethanol (EPA).

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra were measured by a Spex Fluorolog-2 F112AI spectrofluorimeter.

Dilute solutions (absorbance < 0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric measurements. The emission and photoreaction quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}), except when otherwise indicated. 9,10-diphenylanthracene in cyclohexane was used as fluorimetric standard ($\phi_F = 0.90$ in deaerated solvent[20]). For photochemical measurements (potassium ferrioxalate in water as actinometer), a 150 W high-pressure xenon lamp coupled with a monochromator was used. The photoreaction (solute concentrations $\sim 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with analytical Simmetry C18 (4.6 × 250 mm; 5 μm) or Prontosil 200−3-C30 (4.6 × 250 mm; 3 μm) columns and UV detector. Water/acetonitrile mixtures were used as eluents. The monitoring wavelength was at the isosbestic point (when possible), otherwise corrections for different absorption coefficients were introduced. The conversion percentage was held at below 8% to avoid the competition from the back photoreaction.

Sensitized experiments were carried out using biacetyl in benzene as triplet donor.

Fluorescence lifetimes were measured by an Edinburgh Instrument 199S spectrofluorimeter, using the single photon counting method, and a Spex Fluorolog-τ2 apparatus, based on the phase modulation technique. The triplet state was investigated by nanosecond laser flash photolysis. For direct (355 nm) and benzophenone-sensitized (308 nm) measurements, a Continuum Surelite II Nd:YAG laser and an excimer laser (Lambda Physik, LPX 105), respectively, were used.

All measurements were carried out in deaerated solutions by purging with nitrogen. The parameters reported in the tables are averages of at least three independent experiments with mean deviation of ca. 15% for fluorescence quantum yields and lifetimes and ca. 10% for the photoisomerization quantum yields. In the latter case, the error limit can reach 20% for yields smaller than 0.02. Further details on spectrophotometric, fluorimetric, and laser flash photolysis measurements are reported elsewhere.[17,21]

Theoretical Calculations. These were performed using the HyperChem computational package (version 6.1). The calculated electronic spectra (transition energy and oscillator strength) were obtained by ZINDO/S using optimized geometries (according to the PM3 method). Calculations of the configuration interaction included 81 (9 × 9) single excited configurations. The ground state properties, such as dipole moment, heat of formation, and dihedral angles between the ethenic bridge and the side or central aromatic rings were also obtained (see Table S2, Supporting Information). Only conformers derived from rotation of the side aza-aromatic groups have been generally considered. Literature information[1] and our findings from the present work for the hydrocarbon indicate that rotation around single bonds to the central 1,4-substituted benzene ring does not lead to species with significantly different properties. The opposite behavior is obviously displayed by the compound with the central pyridine ring; see below.

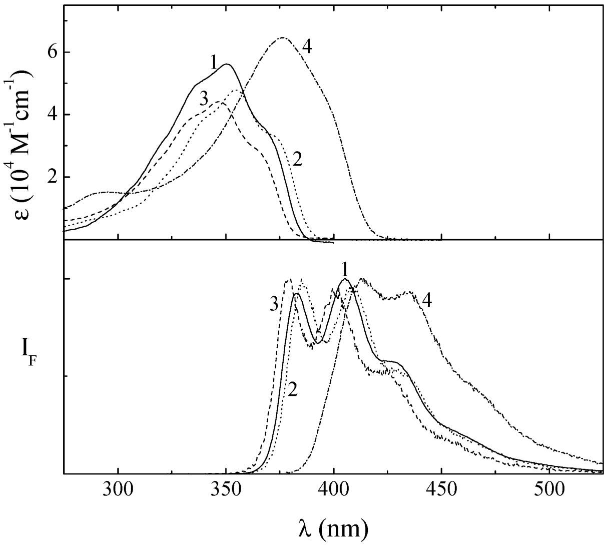


Figure 1. Absorption and normalized fluorescence spectra of the *EE* isomers of (St)$_2$B (—, 1), (2PE)$_2$B (···, 2), (4PE)$_2$B (- -, 3) and (2QE)$_2$B (·-·, 4) in MCH/3MP at room temperature.

Results and Discussion

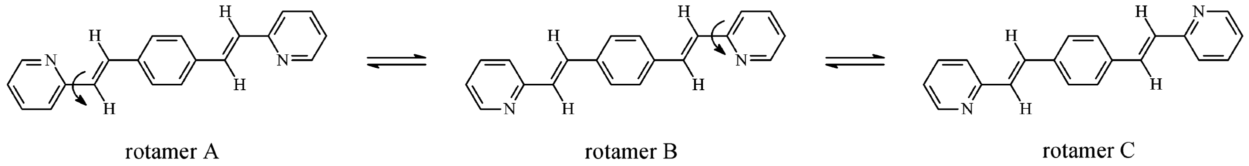
Spectral Properties of the *EE* Isomers. The absorption and normalized emission spectra of the *EE* isomers of the aza-compounds with Ar = 2′-pyridyl (2P), 4′-pyridyl (4P), and 2′-quinolyl (2Q), (see Figure 1 and Table 1) are similar to those of the parent hydrocarbon, *EE*-1,4-(St)$_2$B. A clearer resolution was observed in the fluorescence spectra, with a vibronic progression of $\sim$1400 cm^{-1}, associated with the C=C stretch mode. As observed for styrylpyridines,[11,14−16] the spectra of the 4P derivative are blue-shifted compared to the 2P analogue (see below). The 2P and 2Q derivatives show another absorption band at higher energies (observed as a shoulder around 290 nm for 2P and better resolved, with a maximum at 289 nm, for

TABLE 1: Spectral Properties[a] of the *EE* Isomers of $(St)_2B$ and Three Aza-Derivatives in MCH/3MP at Room Temperature

Ar	absorption λ_{max} (nm)	absorption ϵ_{max} (M^{-1} cm^{-1})	fluorescence λ_{max} (nm)	Stokes shift (cm^{-1})
phenyl	335^{sh}, *350.5*, 369^{sh}	56 150	383, *405.5*, 429^{sh}, 463^{sh}	950
2P	339^{sh}, *354.5*, 373^{sh}	47 830	*386*, 408.5, 433^{sh}, 466^{sh}	870
4P	332^{sh}, *348*, 366^{sh}	44 680	*379*, 401, 425^{sh}, 456^{sh}	940
2Q	289^{sh}, *376*, 397^{sh}	64 630	*413*, 434.5, 466^{sh}	940

[a] The main maxima are in italics; shoulders are indicated with sh.

CHART 2



2Q); these are typical of azastilbenes that have the heteroatom in the ortho position.[22]

The results of the calculations for the most elongated rotamer of each stereoisomer are reported in Table S2. For the 2P derivative, the calculations were carried out for two extreme situations (rotamers A and C of Chart 2) to show the appearance of the second hypsochromic band in compounds bearing the heteroatom in the ortho position with respect to the ethenic bridge. This occurs clearly for rotamer A (favorable distance between N and the ethenic H, as required for the occurrence of the second band[22]), but not for C, with B representing an intermediate situation.

The relatively small Stokes shift indicates that the state reached by excitation and the emitting state have the same nature. The allowed character of the $S_1 \rightarrow S_0$ transition is confirmed by the high values of the radiative kinetic parameter, k_F (see below). In addition, the calculated electronic spectra showed that the first $S_0 \rightarrow S_1$ transition is allowed with a high oscillator strength ($f \sim 2$ for *EE* isomers, see Table S2).

Variation of λ_{exc} produced some changes (rather small but outside of the experimental error) in the emission spectra and quantum yields, but the fluorescence decay remained practically monoexponential. Taken together, these results indicate that the conformational equilibrium is shifted toward the more stable species or, more probably, that the expected conformations,[23,24] due to rotation around the single bonds of the ethene carbons with the central ring or of the side aza groups with the ethenic carbons, have similar photophysical parameters, as reported for the parent hydrocarbon[1] and for styrylpyridines.[25]

The presence of the asymmetric polycyclic group in the quinolyl derivative allowed clear spectral evidence of conformational equilibria to be obtained for this compound (see Figure 2), as expected by analogy with the corresponding 2-styrylquinoline[26] and 2-styrylnaphthalene.[27,28] Some evidence of conformers was also found for the other asymmetric compound, *EE*-2,5-distyrylpyridine (see below).

Photoisomerization of EE Isomers. Table 2 shows the photophysical and photochemical properties of the compounds investigated. The photobehavior of the hydrocarbon, tetrasubstituted by *tert*-butyl groups at the 3′,5′ positions of the side phenyl groups, was studied in the lowest singlet[1,3−5,9] and triplet[6,7] states, both experimentally and by quantum mechanical calculations of the surface profile.[4,6]

As stated above, the excited-state properties of the unsubstituted parent molecule were now measured under our experimental conditions in order to allow a more reliable comparison with the pyridyl derivatives.

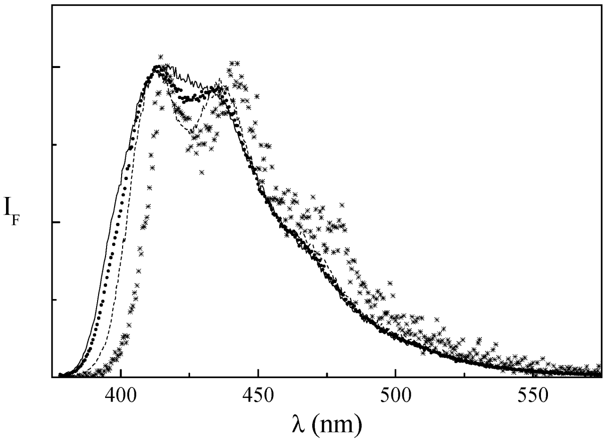


Figure 2. Normalized emission spectra of *EE*-$(2QE)_2B$ in MCH/3MP at room temperature [λ_{exc} = 358 nm (—), 376 nm (···), 400 nm (- -) and 422 nm (∗)].

TABLE 2: Photophysical and Photochemical Parameters of the *EE* Isomers of $(St)_2B$ and Three Aza-Derivatives in MCH/3MP at Room Temperature

Ar	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})	$\phi_{EE\rightarrow ZE}$	$\phi^{sens}_{EE\rightarrow ZE}$ [a]
phenyl	0.84	1.7	4.9	<0.001	0.27
2P	0.32	0.61	5.3	0.25	0.075
4P	0.21	0.54	3.9	0.32	0.26
2Q	0.63	0.74	8.5	0.030[b]	0.040

[a] In benzene. [b] In toluene.

A diabatic mechanism [$^1EE^* \rightarrow {}^1pE^* \rightarrow {}^1pE \rightarrow \alpha\ {}^1ZE + (1-\alpha)\ {}^1EE$], characteristic of *E*-stilbene and many stilbenoid compounds,[28] has been hypothesized for photoisomerization which involves only one double bond (no sign of direct formation of *ZZ* was obtained by irradiation of the *EE* isomers of the aza-derivatives, as reported for the hydrocarbon[4,9]). The mechanism implies internal conversion from the twisted perpendicular configuration in S_1 ($^1pE^*$) to the ground-state surface (^1pE) and equipartitioning ($\alpha \cong 0.5$) to the *EE* and *ZE* ground-state isomers.

While the predominant relaxation pathway of $(St)_2B$ (as also reported for the alkyl-substituted compound[4,5]) is the radiative one, accompanied by a very low isomerization yield and substantial $S_1 \rightarrow S_0$ internal conversion (IC) (evidence of negligible $S_1 \rightarrow T_1$ intersystem crossing, ISC, was obtained by laser flash photolysis experiments carried out in the present work), the heteroatom strongly increases the isomerization yield to the detriment of the radiative deactivation. In fact, a net

TABLE 3: Temperature Effect on the Photophysical and Photochemical Parameters of *EE* Isomers of $(St)_2B$ and Three Aza-Derivatives in MCH/3MP (the Corresponding Arrhenius Parameters Are Reported in the Last Two Rows)

	$(St)_2B$		$(2PE)_2B$			$(4PE)_2B$	$(2QE)_2B$	
T (K)	τ_F (ns)	$\phi_{EE\to ZE}$	ϕ_F	τ_F (ns)	$\phi_{EE\to ZE}$	τ_F (ns)	τ_F (ns)	$\phi_{EE\to ZE}{}^a$
353	1.97	0.034	0.11	0.26	0.43	0.24	0.39	0.19
338	1.87							
333			0.16	0.34	0.40	0.34	0.53	
323	1.78	0.0081					0.58	0.10_5
313			0.23	0.44	0.36	0.45	0.63	
308	1.71							
293	1.63	0.000 84	0.32	0.63	0.25	0.54	0.73	0.033
273	1.50		0.46	0.79			0.84	
253	1.37		0.57	0.90		0.84	0.90	
233	1.24		0.64	1.00			0.90	
213	1.13		0.58	0.96		0.93	0.87	
200						0.95	0.91	
A (10^{13} s^{-1})			1.6	0.20	0.35	0.56	2.1	
ΔE (kcal mol^{-1})	>10	(≈12)	5.7	4.5	4.8	5.2	6.7	(≈8)

[a] In toluene.

decrease in both ϕ_F and τ_F was observed for the three compounds investigated. The radiative kinetic parameter, k_F, remains practically unchanged at values above 10^8 s^{-1}, typical of allowed transitions. The nitrogen effect in the conjugative position leads to a redistribution of the excitation energy which reduces the order of the isomerizable bonds, thus lowering the torsional barrier and favoring the production of *ZE* for both the 2P and 4P compounds. Surprisingly, the $\phi_{EE\to ZE}$ value of the 2Q derivative showed only a small increase in reactivity with respect to that of the hydrocarbon (<0.001). The value in nonpolar solvent reported in Table 2 (0.03) is higher than that reported in CH_3Cl (0.01).[29] The fluorescence parameters of this compound are slightly higher than those of the pyridyl analogues but not enough to compensate for the low photoreactivity. An important increase in the IC quantum yield (ϕ_{IC}) is probably operative. The sensitized reaction also has a very low quantum yield (0.04), which reflects the presence of a large torsional barrier even in T_1, which inhibits the photoreaction and favors relaxation through $T_1 \to S_0$ ISC. It should be recalled that the replacement of a phenyl group of stilbene[12,28] with 2-naphthyl[30,31] and 2-quinolyl[32] groups led to a decrease in the $E \to Z$ photoisomerization quantum yield from 0.48 to 0.16 and 0.11, respectively. In the case of 2-styrylquinoline,[32] the low photoreactivity was explained by the formation of intramolecular (hydrogen-type) bonds between the ortho nitrogen atom and the olefin hydrogens; such N···H interaction is expected to force the excited molecule into a transoid conformation which decays by IC. This was confirmed by the finding that protic solvents and, even more, protonation of the heteroatom led to a much higher photoreactivity.[26] A recent report about the solvent effect on the photophysics of the 4-quinoline analogue (4Q) of our compounds, which displays properties that are quite similar to those of 2Q, pointed out that these compounds are particularly sensitive to hydrogen bonding.[33] In 4Q the intermolecular H-bond prevails, as indicated inter alia by the net decrease of the radiative decay in proton-donating solvents, but the intramolecular one could prevail in 2Q in nonpolar solvents. In any case, the reason twisting is so drastically prevented on going from pyridyl to quinolyl derivatives remains an open question.

The temperature effect on the fluorescence lifetime of *EE* gave energy barriers of about 5 kcal mol^{-1} for the activated process of the 2P and 4P derivatives and 6.7 kcal mol^{-1} for the 2Q derivative (Table 3). In the latter case, where a conformer mixture exists in solution, a temperature change can affect both the rate of twisting and the relative abundance of conformers. For the hydrocarbon, the lifetime did not decrease on increasing temperature, thus implying that its torsional barrier is much higher (>10 kcal mol^{-1}). The unusual decrease of τ_F with temperature, observed in the case of $(St)_2B$, was previously reported for other flexible stilbenelike molecules and related to a viscosity-induced increase of planarity which increases the probability of the radiative transition.[20] However, a temperature-dependent contribution of different rotamers having similar lifetimes cannot be excluded.

Preliminary results of laser flash photolysis on *EE* isomers ruled out a significant role of the triplet state in the overall photoisomerization. Direct excitation produced a very low population of the transient assigned to the triplet state ($\lambda_{max} \sim$ 490 nm, $\phi_T < 0.03$ for all the investigated compounds).

Arrhenius parameters, similar to those obtained from fluorescence data, were found by following the photoisomerization quantum yield of the 2P derivative as a function of temperature, assuming a diabatic singlet mechanism for the $EE \to ZE$ process [${}^1k_{EE\to pE}(T) = 2\phi_{EE\to ZE}(T)/\tau_F(T)$], thus confirming that isomerization was the only activated process. A significant increase in the photoisomerization quantum yield of the 2Q derivative and the hydrocarbon was only observed above room temperature, in agreement with their higher torsional barriers in S_1 (see Table 3).

Spectral Properties and Photoisomerization of *ZE* and *ZZ* Stereoisomers. Figure 3 shows the absorption and normalized emission spectra of the three stereoisomers of 1,4-$(St)_2B$ and its aza-derivatives. The absorption spectrum shifts to the blue and loses intensity and structure on increasing the number of the *Z* double bonds, due to steric hindrance which induces nonplanar conformations and a consequent destabilization. The spectral trend was confirmed by the theoretical calculations which gave quasi-planar and markedly distorted structures for compounds in trans and cis geometries, respectively, as previously reported for the hydrocarbon.[4]

As an example, the calculations for the most elongated conformations of 2P gave the following results: (i) the *EE* isomer is almost completely planar; (ii) for the *ZZ* isomer, the dihedral angles between the side rings and the ethenic bridge are ∼ 40° and those between the ethenic bridge and the central ring are ∼ 65°; (iii) for *ZE*, the central torsion angles are 62.7 and 0.1° and the outer torsion angles are 53.8 and 1.3°. Detailed results for all the compounds are reported in Table S2. The *EE* isomer was always the most stable, followed by *ZE* and *ZZ*. For the 2P derivative, the heat of formation (kcal mol^{-1}) was 112.7 for *EE*, 116.9 for *ZE* and 120.8 for *ZZ*. These values were obtained for the most stable of the various elongated conforma-

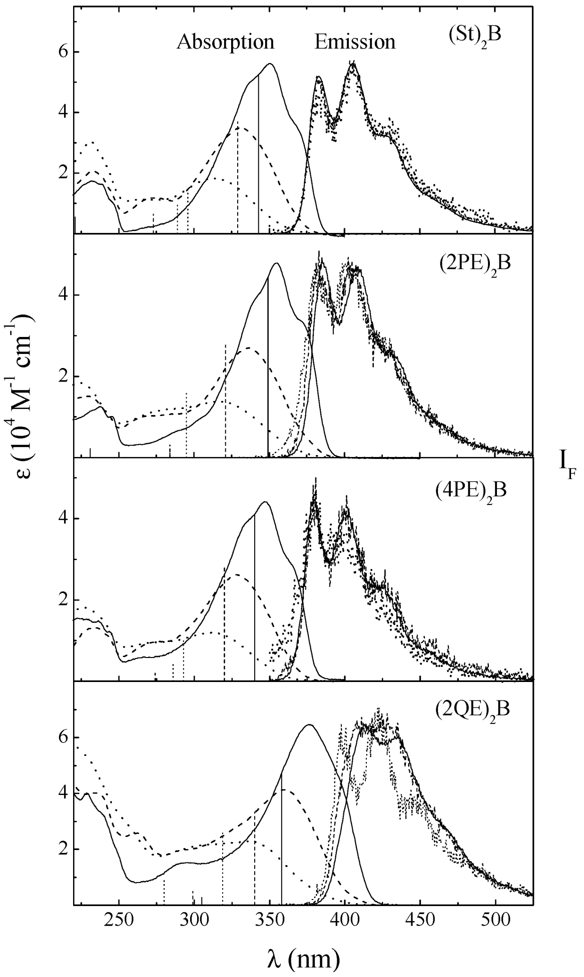


Figure 3. Absorption and normalized fluorescence spectra observed by excitation of the three stereoisomers of (St)$_2$B and their aza-derivatives in MCH/3MP at room temperature: *EE* (—), *ZE* (- -), and *ZZ* (···). Bars indicate the computed intensities.

tions originating from the unfree rotation around quasi-single bonds between the ethenic bridge and the central or side rings. However, it should be noted that the differences between the conformers were very small (<0.5 kcal mol^{-1}), except for the conformers of the *ZE* and *ZZ* isomers of the 2P and, even more, for the 2Q derivatives where rotation of an asymmetric polycyclic group was involved.

The emission spectra recorded under irradiation of the three stereoisomers at room temperature practically overlap one another, while the excitation spectra overlap their respective absorption spectra, indicating that excitation of *ZE* and *ZZ* leads to the direct formation of *EE* in the excited state through an adiabatic mechanism ($^1ZZ^* \rightarrow {}^1ZE^* \rightarrow {}^1EE^*$). Only the fluorescence spectrum recorded under excitation of *ZZ*-(2QE)$_2$B appeared to be rather different (more structured and blue-shifted) from that of the *EE* isomer. However, the available spectral and kinetic information seem to exclude an intrinsic emission from *ZZ*, at least at room temperature; the observed spectrum can be related to particular *EE* conformations of quasi-planar geometry, as indicated by the structured spectrum. A more refined study of the conformer properties of the 2Q compound, based on fluorimetric and statistical analyses,[24] is in progress to get a better understanding about the rotamer-specific adiabatic photoreactivity of the *ZZ* isomer.

An attempt to observe the real emission spectra of *ZE* and *ZZ* was carried out at low temperatures to inhibit twisting. Figure 4 shows the spectra obtained by irradiation of (St)$_2$B in MCH/3MP at 113 K. While excitation of *EE* gave a structured emission spectrum, similar to that at room temperature, *ZE* gave a broad band centered at 430 nm, which was already observable at 170 K. On the other hand, the intrinsic emission spectrum of *ZZ* was not detectable. Even in the rigid matrix at 80 K, the observed spectrum rapidly evolved toward *ZE* and *EE*, indicating a practically barrierless torsional process. The lifetime of *ZE* increased as temperature decreased. The decay profile, which was biexponential at room temperature (Table 4), became practically monoexponential below ~ 210 K (τ_F = 1.6 ns, ϕ_F ~ 0.16), when the adiabatic twisting was inhibited.

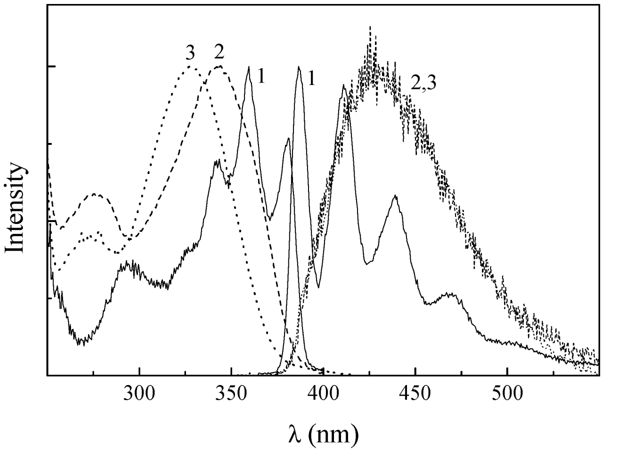


Figure 4. Normalized excitation/absorption and emission spectra of the three stereoisomers of (St)$_2$B in MCH/3MP at 113 K: *EE* (—, 1), *ZE* (- -, 2), and *ZZ* (···, 3).

TABLE 4: Photophysical and Photochemical Parameters Obtained by Excitation of the *ZE* Isomers of (St)$_2$B and Three Aza-Derivatives in MCH/3MP at Room Temperature

Ar	ϕ_F	τ_F (ns)	$\phi_{ZE \rightarrow EE}$
phenyl	0.30	0.58/1.6	0.30
2P	0.11	0.74	0.48
4P	0.02	0.61	0.36
2Q	0.18	0.67	0.28

TABLE 5: Photophysical and Photochemical Parameters Obtained by Excitation of the *ZZ* Isomers of (St)$_2$B and Three Aza-Derivatives in MCH/3MP at Room Temperature

Ar	ϕ_F	τ_F (ns)	ϕ_{ISO}
phenyl	0.021	0.30/1.8	0.053 (*ZZ* → *ZE*) 0.026 (*ZZ* → *EE*)
2P	0.016	0.95	0.24 (*ZZ* → *ZE*) 0.10 (*ZZ* → *EE*)
4P	0.003	0.58	0.33 (*ZZ* → *ZE*) 0.041 (*ZZ* → *EE*)
2Q	0.03	0.72	0.23 (*ZZ* → *ZE*) 0.10 (*ZZ* → *EE*)

Unfortunately, formation of association products of the aza-derivatives[34] in MCH/3MP solutions below 173 K prevented us from measuring the intrinsic fluorescence spectrum and yield of the aza-derivatives in this solvent. For 2P, broad emission bands shifted to the red with respect to the monomer and long lifetimes (~ 25, 10, and 1 ns, for *EE*, *ZE*, and *ZZ*, respectively) were observed. Tables 4 and 5 report the fluorescence yields and lifetimes and the photoisomerization yields measured by excitation of the *ZE* and *ZZ* isomers, respectively.

Low-temperature measurements on the 2P derivative were then carried out in EPA mixture to avoid such an aggregation process. The spectral behavior was similar to that found for the hydrocarbon in MCH/3MP. For the *EE* isomer, both excitation and emission spectra in EPA displayed a resolved vibronic

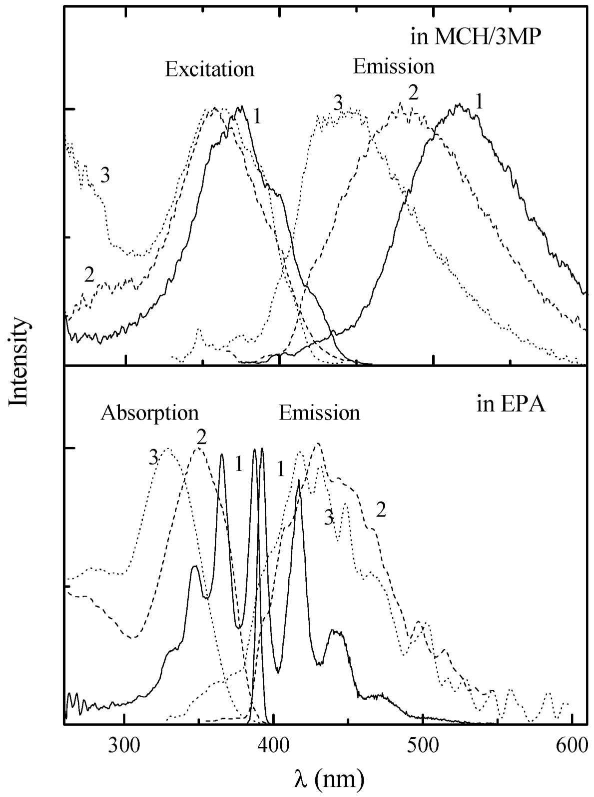


Figure 5. Normalized excitation/absorption and emission spectra observed by excitation of the three stereoisomers of (2PE)$_2$B at 80 K in MCH/3MP and in EPA: *EE* (—, 1), *ZE* (- -, 2), and *ZZ* (···, 3).

structure. Figure 5 shows the fluorescence spectra obtained in the two solvents at 80 K.

The *ZE* spectrum was only detectable in the rigid matrix; however, it rapidly moved toward that of *EE*. The intrinsic fluorescence spectrum of *ZZ* was not detectable even under these conditions; only a growing emission, which rapidly evolved toward *ZE* and *EE*, was observed. This behavior indicates that the aza-derivatives twisted even in the rigid matrix. Their torsional rates then were higher than those of the corresponding hydrocarbon isomers which, in turn, are probably higher than those of the alkyl-substituted analogues, where all three geometrical isomers were identified in the decay profile of *ZZ* and characterized at 153 K.[4] The study of fluorescence decay provided further information about the adiabatic contribution to the photoisomerization mechanism. In the case of the hydrocarbon, the *ZE* fluorescence followed a biexponential decay and the lifetime of the longer-lived component was practically coincident with that of the *EE* isomer. The negative preexponential factor of the short-lived component, assigned to $^1ZE^*$, indicated that this species was a precursor of the emitting $^1EE^*$. Also for the *ZZ* isomer, the decay was well fitted by a biexponential function with a longer lifetime corresponding to *EE* and a short component of about 0.3 ns, with a negative amplitude, which was reasonably assigned to *ZZ*. The coincidence of the emission spectra recorded under excitation of *ZE* and *ZZ* with those of *EE* and the initial growing up of their decays indicate that their intrinsic fluorescence is undetectable at room temperature. On the contrary, as said above, the experimental emission spectrum of the alkyl-substituted 1,4-(St)$_2$B was found to be the sum of the different contributions and bi- and triexponential decays were observed by irradiation of *ZE* and *ZZ*, respectively.[4]

The ϕ_F values measured by excitation of the *ZE* and *ZZ* isomers of the aza-derivatives were substantially lower than those of the hydrocarbon, particularly for the 4P derivative. Very small yields were found for the *ZZ* isomers. The fluorescence decays observed by excitation of the three stereoisomers of these aza-compounds were practically monoexponential with very similar lifetimes for the three stereoisomers and the three compounds. The measured lifetime of 2P increased slightly on going from *EE* to *ZE* and *ZZ*; this unexpected trend could have been caused by some role played by similar rotamers, as revealed by the small dependence of spectra on λ_{exc}. In other words, the measured lifetimes were probably the mean values from various rotamers.

With respect to photoreactivity, the *ZE* isomer had a high isomerization yield to *EE*, particularly for the 2P derivative, which could explain why it was not possible to detect its intrinsic emission at room temperature. Irradiation of *ZZ* led to both *EZ* and *EE* isomers showing that a "one photon−two bond" adiabatic mechanism (direct conversion from *ZZ* to *EE*) was operative. The introduction of the heteroatom in *ZZ* compounds increased the reactivity by reducing the torsional energy barriers, as in the case of *ZE* and *EE*. However, the $\phi_{ZZ\rightarrow ZE}/\phi_{ZZ\rightarrow EE}$ ratio increased (from ~2 for the hydrocarbon to ~8 for 4P) which showed that the adiabatic pathways contributed less to the overall isomerization of the aza-derivatives. The quantum yield of the $ZZ \rightarrow ZE$ adiabatic process can be evaluated by the following equations:

$$^{1}\phi^{\mathrm{ad}}_{ZZ\rightarrow ZE^*} = \frac{\phi_{ZZ\rightarrow EE}}{\phi_{ZE\rightarrow EE}} \tag{1}$$

$$^{1}\phi^{\mathrm{ad}}_{ZZ\rightarrow ZE} = {}^{1}\phi^{\mathrm{ad}}_{ZZ\rightarrow ZE^*}\phi_{\mathrm{G},ZE} \tag{2}$$

where $\phi_{\mathrm{G},ZE}$ is the overall quantum yield of the nonreactive deactivation to the ground state for the *ZE* isomer, given by $(1 - \phi_{ZE\rightarrow EE})$. The results obtained for the investigated compounds are reported in Table 6. The comparison between the calculated (singlet) adiabatic contribution ($^{1}\phi^{\mathrm{ad}}_{ZZ\rightarrow ZE}$) and the experimental value ($\phi^{\mathrm{exp}}_{ZZ\rightarrow ZE}$) for the $ZZ \rightarrow ZE$ photoisomerization shows that these two parameters were practically the same for the hydrocarbon and the 2Q derivative. These results indicate that the adiabatic singlet pathway was the only one that was operative in the $ZZ \rightarrow ZE$ direct photoisomerization process of these two compounds. On the contrary, diabatic contributions of 0.13 and 0.26 were found for the 2P and 4P derivatives, respectively, by the following equation:

$$^{1}\phi^{\mathrm{d}}_{ZZ\rightarrow ZE} = \phi^{\mathrm{exp}}_{ZZ\rightarrow ZE} - {}^{1}\phi^{\mathrm{ad}}_{ZZ\rightarrow ZE} \tag{3}$$

For these two pyridyl derivatives, a mixed adiabatic/diabatic mechanism was also operative in the $ZE \rightarrow EE$ direction. If the fluorescence quanta emitted under *ZE* excitation only come from the adiabatically produced $^1EE^*$, as indicated by the fluorescence spectra and decays, one could calculate a maximum value for the adiabatic contribution to the $ZE \rightarrow EE$ photoisomerization ($^{1}\phi^{\mathrm{ad,max}}_{ZE\rightarrow EE}$) by the ratio of the fluorescence yields measured under excitation of *ZE* and *EE*:

$$^{1}\phi^{\mathrm{ad,max}}_{ZE\rightarrow EE} = \left(\frac{\phi_{\mathrm{F},ZE}}{\phi_{\mathrm{F},EE}}\right)\phi_{\mathrm{G},EE} \tag{4}$$

where $\phi_{\mathrm{G},EE}$ is again estimated by $(1 - \phi_{EE\rightarrow ZE})$. The value of the left-hand side of eq 4 was lower than the overall experimental quantum yield (see Table 6), implying a contribution of diabatic pathway, particularly for the 4P derivative.

TABLE 6: Deactivation Quantum Yields of the Different Isomers of $(St)_2B$ and Three Aza-Derivatives, Calculated from Eqs 1, 2, and 5, Compared with the Experimental Quantum Yields in MCH/3MP at Room Temperature

Ar	$\phi_{G,ZE}$	${}^1\phi^{ad}_{ZZ\to ZE^*}$	${}^1\phi^{ad}_{ZZ\to ZE}$	$\phi^{exp}_{ZZ\to ZE}$	$\phi_{G,EE}$	${}^1\phi^{ad,max}_{ZE\to EE^*}$	${}^1\phi^{ad,max}_{ZE\to EE}$	$\phi^{exp}_{ZE\to EE}$	ϕ^{max}_{F}
phenyl	0.70	0.087	0.061	0.053	~1	0.36	0.36	0.30	0.026
2P	0.52	0.21	0.11	0.24	0.75	0.34	0.36	0.48	0.023
4P	0.64	0.11	0.070	0.33	0.68	0.095	0.065	0.36	0.002
2Q	0.72	0.36	0.25	0.23	0.97	0.29	0.28	0.28	0.066

From the parameters derived above, the limiting value of the radiative contribution from ${}^1EE^*$, obtained by irradiation of *ZZ*, could be derived:

$$\phi_F^{max} = {}^1\phi^{ad}_{ZZ\to ZE^*}\,{}^1\phi^{ad,max}_{ZE\to EE^*}\phi_{F,EE} \tag{5}$$

The very low calculated values (Table 6) are very similar to the total fluorescence quantum yields measured by irradiation of *ZZ* isomers. This result could explain the fact that, under excitation of *ZZ*, only monoexponential decay was observed for the aza-derivative and only biexponential decay for the hydrocarbon (see above).

Photobehavior When the Heteroatom Is in the Central Ring. The observed photobehavior was compared with that of compounds bearing the heteroatom in the central ring. This aspect was previously investigated on 2,6-distyrylpyridine [2,6-$(St)_2P$], a compound where the styryl substituents are in the meta position (cross-conjugation).[19] In that case, the general trend of the photobehavior was rather similar to that of the parent hydrocarbon, the cross-conjugated 1,3-distyrylbenzene [1,3-$(St)_2B$],[1,10,19] but some small differences cannot be neglected. The aza-analogue displayed higher fluorescence, isomerization, and ISC quantum yields, a higher radiative rate constant and a smaller internal conversion quantum yield.[19] However, the validity of a comparison of this behavior with that reported above for the compounds with linear conjugation is questionable because structures and properties of the two series of compounds are quite different. The main differences displayed by the cross-conjugated compounds were as follows: (i) a much higher contribution of the $S_1 \to S_0$ internal conversion to the S_1 deactivation, (ii) clear evidence of at least two conformers, and (iii) the forbidden character of the lowest excited singlet state for 1,3-$(St)_2B$[1], at least for the longer lived hypsochromic conformer.[19]

To have a more valid comparison, we examined the effect of the heteroatom in the central ring for a compound which keeps the linear conjugation of 1,4-$(St)_2B$, namely the asymmetric 2,5-distyrylpyridine [2,5-$(St)_2P$]. As in the case of the crossed conjugated compound, 2,6-$(St)_2P$, the effect of protic solvents on the ^{1}H NMR spectra indicated the presence of intramolecular N···H bonds between the N in the central ring and the close ethenic hydrogen, as shown by the huge shift to higher frequencies of the doublet assigned to H_a on going from benzene, $\delta = 8.07$ ppm and $J = 16.0$ Hz, to DMSO with deuterated water added, $\delta = 7.28$ ppm and $J = 16.2$ Hz (see Table S1).

Figure 6 shows the absorption and emission spectra of the *EE* isomer; they are red shifted with respect to the hydrocarbon because of a more planar geometry of the elongated configuration. The absorption spectrum shows that the second transition (around 300 nm), specific to the *o*-azastilbene analogues,[22] was more intense in the conformer with N close to the ethenic hydrogen (see calculated electronic spectrum in Table S2). The emission spectrum depended on λ_{exc} (see Figure 6). The calculated values of the heats of formation for the four possible conformers of this asymmetric molecule were very similar (105.33−105.69 kcal/mol), suggesting that this compound exists as a mixture of different species with similar abundances in fluid solutions. The biexponential decay experimentally observed indicates the presence of two pairs of similar conformers with $\tau_A = 0.43$ ns (abundance 35%) and $\tau_B = 0.92$ ns (65%) and the experimental quantum yield at $\lambda_{exc} = 354$ nm, $\phi_F{}^{exp} = 0.29$. The longer-lived species has an absorption spectrum shifted to the red, and then the quasi-pure spectrum and fluorescence quantum yield ($\phi_{F,B} = 0.40$ at $\lambda_{exc} = 400$ nm) could be obtained by exciting at the tail of the spectrum.

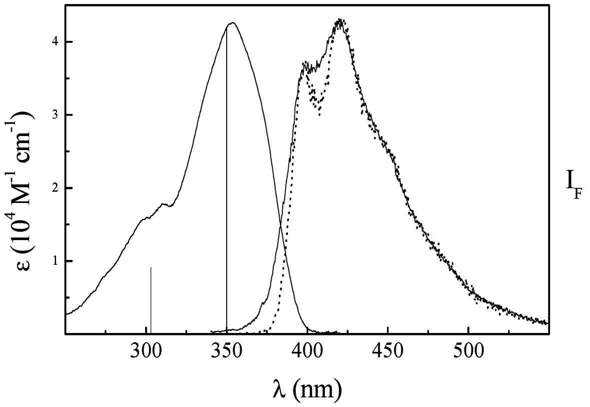
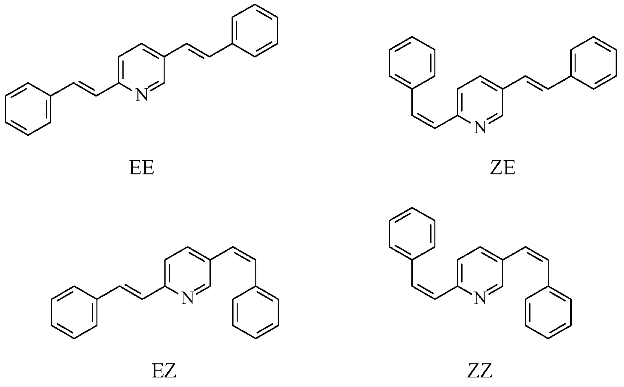


Figure 6. Absorption and normalized fluorescence spectra [$\lambda_{exc} = 336$ nm (—) and 397 nm (···)] of *EE*-2,5-$(St)_2P$ in MCH/3MP at room temperature. Bars indicate the computed intensities.

CHART 3



The direct isomerization of *EE* led to a single product (assigned to *ZE*, see Chart 3, on the basis of the NOESY spectrum, Table S1) with $\phi_{EE\to ZE} = 0.046$, indicating that the rotation of the double bond adjacent to pyridine was faster, as found for pyridylphenylbutadienes.[17,18] In contrast, the biacetyl-sensitized isomerization in the triplet state gave $\phi_{EE\to ZE} = 0.025$ and formed a second photoproduct with a quantum yield of 0.098. The absorption spectrum of the latter overlapped that of *ZE* (the maximum was only slightly red-shifted, by ~1 nm). Even though it was difficult to isolate this second photoproduct for a NMR characterization, it was reasonably assigned to the *EZ* stereoisomer because the calculations indicated that *ZE* and *EZ* have almost identical spectra, as experimentally observed, while the other possible isomer, *ZZ*, is markedly hypsochromic (see Table S2).

Conclusions

The effect of introducing a nitrogen atom into distyrylbenzene on the photobehavior depends on the type of conjugation and the position of the heteroatom. In the case of 1,4-distyrylbenzene (linear conjugation), the presence of nitrogen in the side rings induces a net decrease in the yield of the radiative deactivation and a corresponding increase in the reactive pathway, which is favored by lower torsional barriers in the singlet manifold. In these symmetric compounds, the introduction of N modifies the potential energy surfaces of S_1 for the rotation around the double bonds which lowers the energy barriers to photoisomerization, with the exception of the quinolyl derivative, and, probably, to stabilization of the perpendicular configurations which favors the diabatic pathways in the *ZZ* → *ZE* and *ZE* → *EE* isomerizations.

The triplet state does not seem to play a significant role in the direct photoreaction. Moreover, the triplet formed by sensitization, which led to a good isomerization yield for 4P, had very small yields when the N atom was in the ortho position with respect to the ethene bridge. A reasonable explanation, reported in previous papers,[26,32] is the formation of intramolecular N···H hydrogen-type bonds, which stabilize the molecule in more planar conformations and inhibit the twisting around the double bond. This behavior is probably more important in the triplet than in the singlet manifold.

The results obtained for 2,5-$(St)_2P$ with the heteroatom in the central ring showed that the presence of the nitrogen atom substantially increased the IC to S_0 but only slightly increased the reactivity of S_1, while the radiative deactivation decreased.

In the pyridyl derivatives, it was practically impossible to separate the intrinsic properties of the different rotamers. Clear evidence of conformational equilibria was only obtained for the asymmetric 2,5-$(St)_2P$ and 1,4-$(2QE)_2B$, because rotation of the styryl and the condensed-ring groups, respectively, around the single bonds with the ethenic carbon can produce different rotamers with sufficiently different fluorescence properties. This allowed some intrinsic properties of the two detected species to be obtained by selective excitation.

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Supporting Information Available: Tables of ^1H NMR data useful for the characterization of the geometrical isomers and calculated electronic spectra (transition energy and oscillator strength), dipole moments, heats of formation and dihedral angles between the ethenic bridge and the side or central aromatic rings with text describing the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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